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Foreword

The area of magnetism in solids is of particular significance in the Indian context since Indian scientists were among the earliest to contribute to this important field. Magnetism has both the necessary angles, technological and academic, and has sustained its growth and importance through the development of new materials, techniques and theories. Many new concepts such as dimensionality, superexchange, spin dynamics, magnetic order etc. have emerged in recent years. Indian science however has not contributed its corresponding share to this area recently. This issue of Proceedings (Chemical Sciences) is intended to project some of the present-day chemistry and physics behind magnetism. One would see here a sampling of inorganic solids with interesting magnetic properties and a variety of experimental techniques such as simple magnetic susceptibility measurements (including those of field-cooled and zero-field cooled d.c. susceptibilities), low frequency EPR and neutron diffraction employed to establish magneto-structural correlations.

We have not been able to cover all the important aspects of magnetism and magnetic materials in this issue. We however hope that this issue would be of use to senior practitioners as well as young research scholars.

We thank all the authors for their excellent contributions.

P T Manoharan
Guest Editor

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Neutron diffraction and optical studies of the ionic ferromagnet Rb_2CrCl_4 doped with Mg^{2+} , V^{2+} and Fe^{2+}

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Abstract. Powder and single crystal neutron diffraction and optical spectroscopy are used to study the effect of substituting non-magnetic (Mg^{2+}) or magnetic (V^{2+} , Fe^{2+}) cations on the Cr^{2+} sites in the ionic ferromagnet Rb_2CrCl_4 . Comparison of powder neutron diffraction of Rb_2CrCl_4 and $\text{Rb}_2\text{Cr}_{0.73}\text{Mg}_{0.27}\text{Cl}_4$ shows that the latter still exhibits long range order at 4.2 K with the moments parallel to the basal plane. Single crystal neutron diffraction shows that substituting 11% Mg^{2+} lowers the Curie temperature by 19% and 3% V^{2+} lowers it by 6%. Analysis of satellite fine-structure near the exciton-magnon hot bands in the visible absorption spectra of crystals of Rb_2CrCl_4 doped with V^{2+} and Fe^{2+} leads to estimates of 6.6 K and 5.2 K for the $\text{Cr}^{2+}\text{-V}^{2+}$ and $\text{Cr}^{2+}\text{-Fe}^{2+}$ exchange constants.

Keywords. Neutron diffraction; ferromagnet; doped Rb_2CrCl_4 .

1. Introduction

When a ferromagnet is diluted with non-magnetic ions the spin correlations are reduced and the Curie temperature T_c tends towards zero at a critical concentration of magnetic ions called the percolation limit, below which there are only finite clusters of magnetic ions. Rb_2CrCl_4 is an example of a two-dimensional square planar Heisenberg ferromagnet (Hutchings *et al* 1981) for which the theoretical percolation limit x is 0.59 (Shante and Kirkpatrick 1971). It is therefore of interest to observe the effect of increasing the concentration of both non-magnetic (Mg^{2+}) and magnetic (V^{2+}) dopant ions M^{2+} in $\text{Rb}_2\text{Cr}_x\text{M}_{1-x}\text{Cl}_4$. A convenient way to monitor T_c is to measure the temperature dependence of the magnetic intensity of a suitable reflection by single crystal neutron diffraction, though there is an upper limit to the concentration of dopant ions that can be incorporated into Rb_2CrCl_4 and still allow preparation of large crystals. In this paper we report measurements of T_c for crystals of composition $\text{Rb}_2\text{Cr}_{0.89}\text{Mg}_{0.11}\text{Cl}_4$ and $\text{Rb}_2\text{Cr}_{0.97}\text{V}_{0.03}\text{Cl}_4$. For higher concentrations of dopant ions, where only polycrystalline samples are available, powder neutron diffraction can still indicate the presence of magnetic order. However, the preferred moment direction is not so unambiguously defined as by a single crystal experiment. As well as reporting the powder neutron diffraction of $\text{Rb}_2\text{Cr}_{0.73}\text{Mg}_{0.27}\text{Cl}_4$ at 78 and 4.7 K we have measured and refined powder neutron diffraction profiles of Rb_2CrCl_4 itself for comparison. The magnetic structure of the latter has already been determined by single crystal neutron diffraction (Janke *et al* 1983) so it is of interest to see how clear an

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indication of the moment orientation the powder data gives. We also give a brief account of this method of structure determination.

A further point of interest about Rb_2CrCl_4 is that it is unique among the small group of transparent ionic ferromagnets in having discrete optical absorption bands in the visible region. These bands have been studied in detail both theoretically (Harrop 1981) and experimentally (Janke *et al* 1982). They arise from magnon-exciton combination excitations via the 'hot-band' mechanism (Shinagawa and Tanabe 1971), which involves the coupling of an excitation created by photon absorption to simultaneous annihilation of a thermally populated magnon. Therefore, as the temperature is raised, the intensity of these bands increases with the thermal magnon population. We have shown (Wood *et al* 1982) that when Rb_2CrCl_4 is doped with Mn^{2+} the exciton-magnon bands develop satellite sidebands, whose energy separation from the parent absorption bands depends on the Cr^{2+} - Mn^{2+} exchange constant. Similar spectra of Rb_2CrCl_4 doped with V^{2+} and Fe^{2+} are reported here, together with the spectrum of a crystal doped with Mg^{2+} , which demonstrates that the sidebands arise only from magnetic impurities.

2. Experimental

Crystals of Rb_2CrCl_4 doped with Mg^{2+} , V^{2+} and Fe^{2+} were grown by the method described previously (Walker *et al* 1982). A powder of composition $\text{Rb}_2\text{Cr}_{0.73}\text{Mg}_{0.27}\text{Cl}_4$ was prepared by quickly cooling a molten mixture of RbCrCl_2 and MgCl_2 in a sealed silica ampoule. The ratio of Cr^{2+} to Mg^{2+} in the powder was determined by atomic absorption spectroscopy.

Powder neutron diffraction data were collected on the Dido Curran diffractometer at AERE Harwell using an incident neutron wavelength of 1.37 Å. The sample was contained in a vanadium can and mounted in a CT14 cryostat. Diffraction patterns were recorded at 4.2 K and above T_c . Scans of 2θ from 5° to 90° were employed with 0.1° steps and a counting time of 2 minutes.

The highest concentration of Mg^{2+} found in a single crystal boule was 11% in a Czochralski grown sample whose composition varied from 13% to 10% Mg^{2+} across a 0.75 cm section. The boule consisted of two major crystallites with axes sufficiently well-separated to be treated as distinct crystals. It was aligned on the crystal axes of the larger crystallite in a CT14 cryostat. At each temperature the (0, 0, 4) peak intensity was measured on the Dido MK VI 2 circle diffractometer at AERE Harwell using a neutron wavelength of 1.093 Å. The procedure employed was to carry out a scan of the crystal angle ω followed by an $\omega/2\theta$ scan, the maximum of the latter being taken as the intensity of the peak. This peak intensity was corrected for diffuse scattering and background, measured by making an $\omega/2\theta$ scan at (0, 0, 3.65). The highest concentration of V^{2+} which could be obtained in a single crystal with a small concentration gradient was 3%. The temperature variation of (0, 0, 4) intensity in a crystal of $\text{Rb}_2\text{Cr}_{0.97}\text{V}_{0.03}\text{Cl}_4$ was measured following the same procedure as that used for the Mg^{2+} -doped crystal.

Absorption spectra were measured with a McPherson RS10 high resolution double beam spectrophotometer equipped with an Oxford Instruments CF10 continuous flow helium cryostat.

3. Results and discussion

3.1 Powder neutron diffraction: Rb_2CrCl_4 and $\text{Rb}_2\text{Cr}_{0.73}\text{Mg}_{0.27}\text{Cl}_4$

The Rietveld refinement technique (Rietveld 1969) was employed to determine the nuclear and magnetic structures of pure and Mg^{2+} doped Rb_2CrCl_4 . In this method one assumes that each Bragg diffraction peak is of Gaussian lineshape and fits the calculated profile $Y_{i\text{calc}}$ to the measured profile $Y_{i\text{obs}}$ at each value of the Bragg angle $2\theta_i$. $Y_{i\text{calc}}$ is expressed as

$$Y_{i\text{calc}} = t S_R^2 j_R L_R \frac{2(\ln 2)^{1/2}}{H_R(\pi)^{1/2}} \times \exp[-4 \ln 2 \{2\theta_i - 2\theta_R\}/H_R\}^2, \quad (1)$$

where $Y_{i\text{calc}}$ is the calculated number of counts, S_R is the total structure factor (defined below) for reflection R , H_R is the full width of the peak at half height, L_R is the Lorentz factor, $2\theta_R$ is the calculated Bragg angle of the peak, t is the step width and j_R is the multiplicity of the reflection.

The angular dependence of the halfwidths of the diffraction peaks is expressed as

$$H_R^2 = U \tan^2 \theta_R + V \tan \theta_R + W, \quad (2)$$

where U , V and W are the halfwidth parameters determined from the refinement.

The square of the total structure factor is given as

$$S_R^2 = (F_N^2 + F_M^2 \sin^2 \alpha) \exp[-2B \sin^2 \theta_R / \lambda^2 + G \beta_R^2], \quad (3)$$

where F_N , F_M are the nuclear and magnetic structure factors, α is the angle between the reciprocal lattice vector and the moment direction, B is the overall isotropic temperature parameter, G is the preferred orientation parameter (a measure of the halfwidth of the assumed Gaussian distribution of the normals about the preferred orientation direction) and β is the acute angle between the scattering vector and the normal to the preferred direction of the crystallites.

For a centrosymmetric unit cell $F_{M\text{calc}}$ is expressed in terms of the magnetic vector K as

$$F_{M\text{calc}} = \sum_{\phi} \sum_j \sum_q f_j K_{\phi, j, q} \cos 2\pi(hx_{j, q} + ky_{j, q} + lz_{j, q}), \\ \times \exp(-B_j \sin^2 \theta_R / \lambda^2) \quad (4)$$

where f_j is the form factor, $K_{\phi, j, q}$ (in Bohr magnetons) is the component of the magnetic vector in the ϕ direction ($\phi = x, y, z$; cartesian axes), localised on the j th atom at the q th equivalent position. B_j is the individual isotropic temperature parameter for atom j . The magnetic vector can undergo rotation i.e.

$$\begin{pmatrix} K_{x, j, q} \\ K_{y, j, q} \\ K_{z, j, q} \end{pmatrix} = M_{j, q} \times \begin{pmatrix} K_x \\ K_y \\ K_z \end{pmatrix}, \quad (5)$$

where $M_{j,q}$ is the 3×3 rotation matrix describing the rotation of the magnet vector of the j th atom at the q th equivalent position. $Y_{i\text{obs}}$ is defined as the measured number of counts minus the background counts for the same position minus the monitor count.

The principle of the least squares refinement is to minimise R_p (P = Profile) defined as

$$R_p = 100 \times \sum_i \left| Y_{i\text{obs}} - \frac{1}{C} Y_{i\text{calc}} \right| / \sum_i Y_{i\text{obs}}. \quad (6)$$

Other values obtained are

$$R_N = 100 \times \sum_i \left| F_{N\text{obs},i}^2 - \frac{1}{C} F_{N\text{calc},i}^2 \right| / \sum_i F_{N\text{obs},i}^2, \quad (7)$$

$$R_M = 100 \times \sum_i \left| F_{M\text{obs},i}^2 - \frac{1}{C} F_{M\text{calc},i}^2 \right| / \sum_i F_{M\text{obs},i}^2, \quad (8)$$

where C is the overall scale factor such that $Y_{\text{calc}} = CY_{\text{obs}}$.

The data were fitted using the 'Powder' suite of programmes mounted on the DEC 10 at E.R.C.C., Edinburgh.

Single crystal neutron diffraction studies of Rb_2CrCl_4 have shown that the crystals contain domains of two space groups $Acam$ and $Bbcm$, corresponding to two alternative ways of packing the Jahn-Teller distorted layers. However, in a powder diffraction experiment the reflections from both domains occur at the same 2θ . Hence, the refinement of the powder data can be treated as a one-domain problem. In the present case the $Bbcm$ space group was employed in the structural refinement because the orientation of the crystallographic c -axis coincides with that of the $I4/mmm$ cell of the parent undistorted K_2NiF_4 lattice, and $Bbcm$ notation was used for all (h, k, l) in this paper.

The results of the refinement for the nuclear only and the nuclear and magnetic structures are given in table 1. The coherent scattering lengths used were $b_{\text{Rb}} = 0.71$, $b_{\text{Cr}} = 0.352$, $b_{\text{Cl}} = 0.96$, $b_{\text{Mg}} = 0.52 \times 10^{-12}$ cm, (Bacon 1975). In the refinements the positional parameter of $\text{Cr}11(x)$ was not set equal to $\text{Cr}11(y)$ but both were allowed to vary independently.

Fit 1 (table 1) lists the parameters refined for Rb_2CrCl_4 at 78 K. This temperature is well above T_c (52 K, Hutchings *et al* 1981) and hence only the nuclear structure parameters were refined. Fits 2 to 4 list the refined nuclear and magnetic parameters for Rb_2CrCl_4 at 4.2 K where the $F_{M\text{calc}}$ was calculated from the method used by Halpern and Johnson (1939). The magnetic moment was assumed to be localised in the $\text{Cr}^{2+}3d$ orbital and an isotropic $\text{Cr}^{2+}3d \langle j_0 \rangle$ represented the form factor. An identity rotation matrix (5) operated at the C equivalent positions, thus assuming that the moments are all aligned parallel. In the fit an initial moment direction was chosen i.e. (K_x, K_y, K_z) and the components were varied.

Fit 2 lists the refined parameters when the moment is constrained along $[010]$. This fit is shown in figure 1 with low angle reflections indexed, and the weak $(0, 0, 4)$ reflection used in the following section to monitor the magnetization of the doped compounds by single crystal neutron diffraction can just be detected. Fit

Table 1. Refinements of powder neutron diffraction data for Rb_2CrCl_4 (fits 1-4) and $\text{Rb}_2\text{Cr}_{0.73}\text{Mg}_{0.27}\text{Cl}_4$ (fits 5-6).

Fit number	1	2	3	4	5	6	78	5.5
Temperature (K)	78	4.2	4.2	4.2	4.2	4.2	78	5.5
Initial spin direction	—	0, 1, 0	1, 0, 0	0, 0, 1	0, 1, 0	0, 0, 1	—	1, 1, 0 fixed
Rb (z)	0.3587(4)	0.3580(5)	0.3580(5)	0.3595(5)	0.3560(8)	0.3570(8)	0.3556(18)	0.3568(18)
Cl(2) (z)	0.1540(3)	0.1540(3)	0.1541(4)	0.1539(3)	0.1531(7)	0.1532(6)	0.1510(14)	0.1508(14)
Cl(1) (x)	0.2391(14)	0.2399(19)	0.2399(17)	0.2400(19)	0.2415(36)	0.2417(36)	0.2341(1)	0.2346(1)
Cl(1) (y)	0.2366(11)	0.2343(11)	0.2343(11)	0.2354(13)	0.2344(21)	0.2349(22)	0.2342(1)	0.2346(1)
Rb (B) [$\text{\AA}^2$]	1.07(17)	0.49(23)	0.48(23)	0.76(23)	0.50(34)	0.57(33)	0.47(9)	0.37(5)
Cr (B) [$\text{\AA}^2$]	0.33(26)	0.83(38)	0.81(37)	1.11(41)	0.96(53)	1.11(53)	0.49(16)	0.57(8)
Cl(2) (B) [$\text{\AA}^2$]	1.21(14)	1.20(19)	1.21(19)	1.02(16)	0.86(24)	0.83(22)	1.43(9)	0.59(4)
Cl(1) (B) [$\text{\AA}^2$]	1.02(8)	0.85(11)	0.85(10)	1.06(11)	0.69(13)	0.74(13)	0.48(3)	0.36(3)
K_x	—	0.0	3.8(1)	0.0	0.0	0.0	—	—
K_y	—	3.8(1)	0.0	0.0	2.5(3)	0.0	—	—
K_z	—	0.0	0.0	3.1(1)	0.0	2.38(2)	—	—
Moment [μ_B]*	—	3.8(1)	3.8(1)	3.1(1)	2.5(3)	2.4(2)	—	3.12(34)
a [$\text{\AA}$]	7.211(2)	7.196(2)	7.197(2)	7.197(2)	7.141(6)	7.143(6)	7.183(18)	7.193(18)
b [$\text{\AA}$]	7.185(2)	7.173(2)	7.173(2)	7.172(2)	7.114(6)	7.112(6)	7.183(2)	7.193(18)
c [$\text{\AA}$]	15.698(2)	15.702(2)	15.701(2)	15.701(2)	15.761(6)	15.760(6)	15.67(4)	15.72(4)
Preferred orientation parameter	0.175(6)	0.183(7)	0.187(7)	0.164(7)	0.035(11)	0.022(11)	—	—
R_{Nuclear} (%)	10.31	7.79	7.82	8.81	10.71	10.75	—	—
R_{Magnetic} (%)	—	10.84	10.72	10.91	16.96	17.73	—	—
R_{Profile} (%)	10.31	10.20	10.20	10.91	16.39	17.32	—	—

* Mean moment per metal ion site

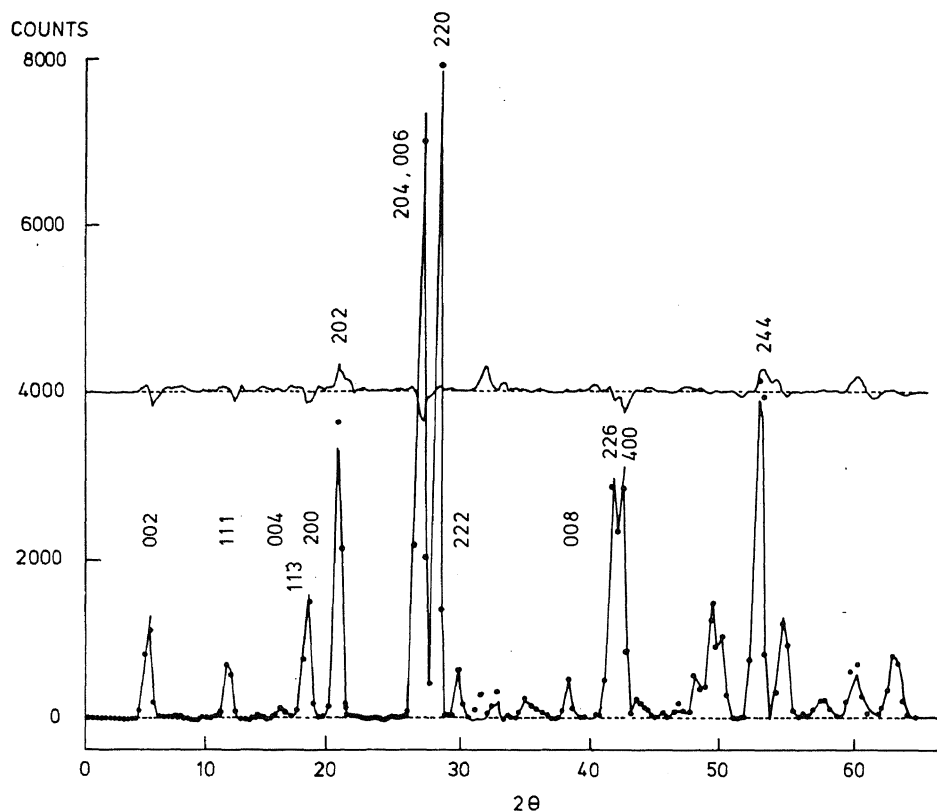


Figure 1. Powder neutron diffraction profile of Rb_2CrCl_4 at 4.2 K. The line through the data points is a fit to a model with the moment constrained along $[010]$ (fit 2, table 1). The difference between observed and calculated profiles is indicated and major reflections are labelled.

indicates that the same final parameters, and insignificantly different R -values, are obtained if the moment direction is constrained to $[100]$, thus confirming that the powder experiment is not sensitive enough to define the direction of the moment within the basal plane since the a and b parameters are almost identical.

However, if the moments are constrained to $[001]$ R_p increases markedly, (fit 4) so that the data clearly indicate that the moments lie in the basal plane. In fact it is known from the single crystal neutron diffraction (Janke *et al* 1983) that the moments are aligned along $\langle 100 \rangle$.

The last two columns of table 1 list the parameters refined by Janke *et al* (1983) from single crystal neutron diffraction data at 78 K and 5.5 K. There is quite good agreement between the lattice constants and positional parameters obtained from both types of measurement. On the other hand, the Debye-Waller factors do not agree so well and for the powder data they have quite high standard deviations. The refined magnetic moment of $3.8(1) \mu_B$ (fit 4) agrees reasonably well with the saturation value of $4.06(1) \mu_B$ obtained from magnetization measurements (Cornelius *et al* 1986).

The magnetic and nuclear structure of a powder of composition $\text{Rb}_2\text{Cr}_{0.73}\text{Mg}_{0.27}\text{Cl}_4$ was refined in the same space group $Bbcm$ setting the scattering length b at the Cr^{2+} site at $0.73b_{\text{Cr}} + 0.27b_{\text{Mg}}$. The refined parameters are given in table 1 and the 4.2 K profile is shown in figure 2. It is worth noting that, in contrast to Rb_2CrCl_4 , inclusion of the preferred orientation parameter has only a small effect on the R_p value, presumably because doping with Mg^{2+} makes the crystals harder to cleave. The magnetic moment of $2.5(3) \mu_B$ (fit 5) agrees quite well with the value of $2.8 \mu_B$ calculated as 73% of that of Rb_2CrCl_4 . Constraining the moments to the $[001]$ direction (fit 6) leads to an increase in R_M suggesting that the moments lie in the basal plane even in the Mg^{2+} doped compound. Doping with Mg^{2+} also increases the c lattice parameter but decreases a and b .

3.2 Single crystal neutron diffraction: temperature dependence of $(0, 0, 4)$

In a ferromagnetically ordered crystal the magnetic contribution to the neutron diffraction intensity is found at the same reciprocal lattice points as that arising from the nuclear scattering. Thus to follow the temperature dependence of magnetic intensity we must select a reflection with a favourable ratio of F_M to F_N . From our earlier single crystal neutron diffraction work on Rb_2CrCl_4 (Janke *et al*

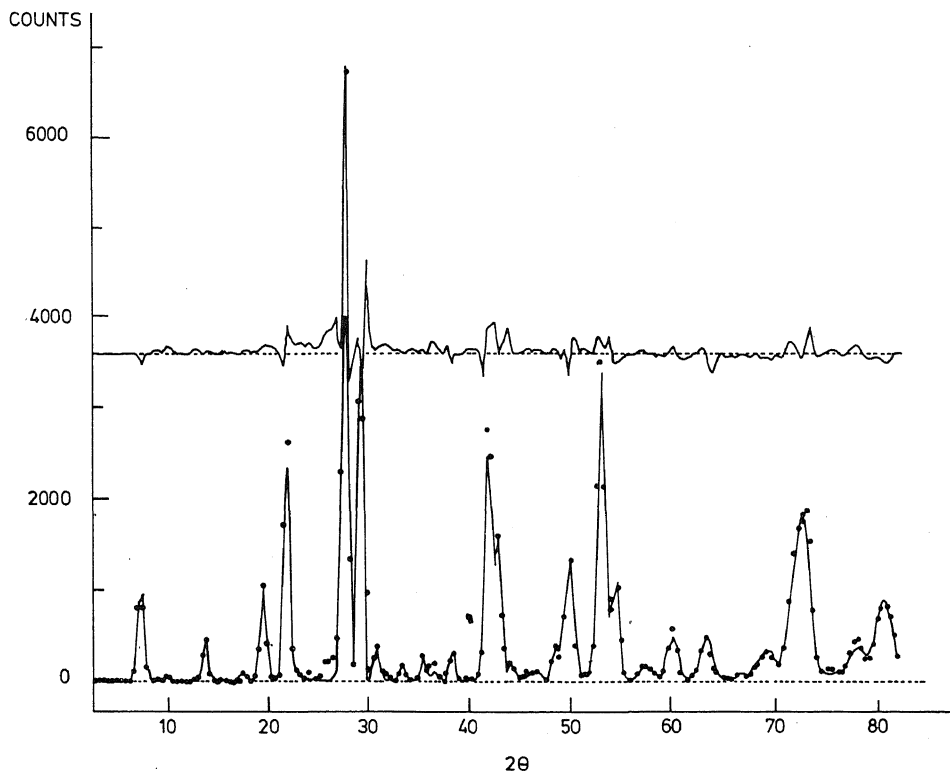


Figure 2. Powder neutron diffraction profile of $\text{Rb}_2\text{Cr}_{0.73}\text{Mg}_{0.27}\text{Cl}_4$ at 4.2 K. The line through the data points is a fit to a model with the moment along $[010]$ (fit 5, table 1). The difference between observed and calculated profiles is indicated.

1983) it was known that the (0, 0, 4) reflection is suitable for this purpose. This arises in part from the fact that Rb_2CrCl_4 is an easy-plane system, so since the scattered intensity

$$I \propto F_N^2 + F_M^2 \sin^2 \alpha, \quad (1)$$

[cf. (1) and (3)] the scattering vector of (0, 0, 4) is perpendicular to the momentum direction. It can also be seen from figure 1 that the nuclear intensity of this reflection is particularly small. From (4) the magnetic structure factor at temperature T

$$F_M(T) \propto \sum_j \sum_q f_j \mu_{j,q}(T), \quad (1)$$

where $\mu_{j,q}(T)$ is the moment residing on the j th atom at the q th equivalent position which becomes zero at T_c .

Results of the measurements of the magnetization of $\text{Rb}_2\text{Cr}_{0.89}\text{Mg}_{0.11}\text{Cl}_4$ and $\text{Rb}_2\text{Cr}_{0.97}\text{V}_{0.03}\text{Cl}_4$ measured in this way are shown as a function of temperature in figure 3. From this figure we see that T_c of the Mg^{2+} doped crystal is 42 K, i.e. substituting 11% of the Cr^{2+} by Mg^{2+} decreases T_c by 10 K or 19%. A comparable proportional decrease in T_c has been found in $\text{K}_2\text{Cu}_x\text{Zn}_{1-x}\text{F}_4$ (Okuda *et al* 1980) a two-dimensional $S = 1/2$ Heisenberg ferromagnet, for which single crystals could be grown at all concentrations from $x = 0$ –1. In addition Kurtz (1982) studied the magnetic properties of $\text{Rb}_2\text{Cr}_x\text{Cd}_{1-x}\text{Cl}_4$ by single crystal magnetometry, and found that in samples containing up to 14% Cd^{2+} , T_c decreased while the saturation moment per Cr^{2+} ion was the same as in Rb_2CrCl_4 . On the latter point, our powder diffraction result for the 27% Mg^{2+} -substituted sample (§ 3.1) leads us to the same conclusion.

Our single crystal neutron diffraction measurements on the V^{2+} -doped crystal (figure 3) indicate T_c as 49.3 K, a value comparable with that observed in $\text{Rb}_2\text{Cr}_x\text{Mn}_{1-x}\text{Cl}_4$ at similar values of x (Munninghoff *et al* 1981). In the latter the Mn^{3+} - Mn^{2+} and Mn^{2+} - Cr^{2+} exchange is antiferromagnetic and in contrast to this situation with Mg^{2+} doping, Munninghoff *et al* (1981) found that on diluting Rb_2CrCl_4 with Mn^{2+} , not only T_c but also the saturation moment per metal ion decreases.

3.3 Optical absorption spectra: sidebands in $\text{Rb}_2\text{Cr}_{0.97}\text{V}_{0.03}\text{Cl}_4$ and $\text{Rb}_2\text{Cr}_{0.95}\text{Fe}_{0.05}\text{Cl}_4$

Further evidence for the antiferromagnetic sign of the Cr^{2+} - Mn^{2+} exchange constant in Mn^{2+} -doped Rb_2CrCl_4 has come from studies of the optical absorption spectrum. Wood *et al* (1982) first observed satellite absorption bands near the 623 nm exciton-magnon combination band in Rb_2CrCl_4 crystals doped with Mn^{2+} . These extra bands were assigned as Cr^{2+} ligand field excitations, which take place with a decrease of spin, accompanied by spin flips on isolated Mn^{2+} , antiferromagnetically coupled to Cr^{2+} neighbours. The Cr^{2+} ground state is $^5B_{1g}$ and the Mn^{2+} is $^6A_{1g}$. Therefore the coupled ground state wavefunction of a Cr^{2+} , Mn^{2+} pair can be written $|G\rangle = |-5/2, 2\rangle = |M_S^{\text{Mn}^{2+}}, M_S^{\text{Cr}^{2+}}\rangle$ where M_S is the magnetic quantum number. Thus the first excited state is $|E_1\rangle = |-3/2, 1\rangle$, the second excited state is $|E_2\rangle = |-1/2, 0\rangle$ and so on.

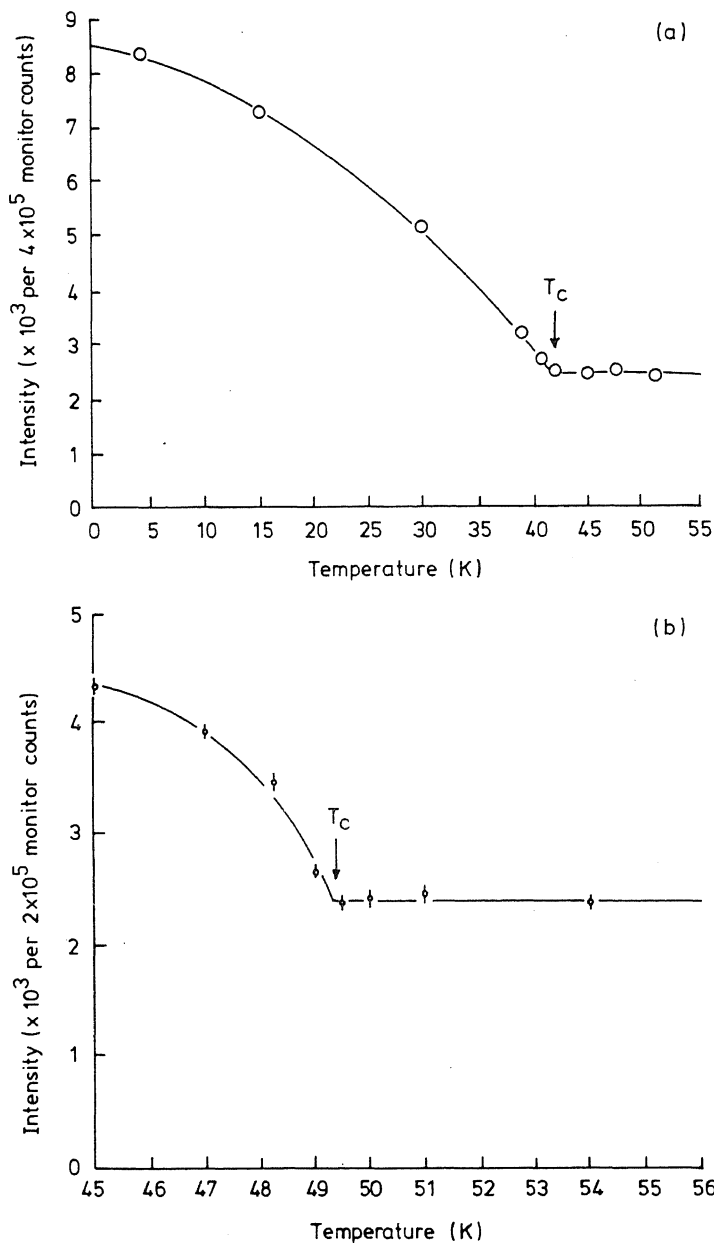


Figure 3. Temperature dependence of the peak intensity of $(0, 0, 4)$ in the single crystal neutron diffraction of (a) $\text{Rb}_2\text{Cr}_{0.89}\text{Mg}_{0.11}\text{Cl}_4$ and (b) $\text{Rb}_2\text{Cr}_{0.97}\text{V}_{0.03}\text{Cl}_4$, corrected for diffuse scattering and background.

To confirm that the sidebands were caused by spin flips of the impurity ions coupled to Cr^{2+} excitons we measured the absorption spectrum of $\text{Rb}_2\text{Cr}_{0.95}\text{Mg}_{0.05}\text{Cl}_4$ since substitution of Cr^{2+} with non-magnetic ions should not introduce any sidebands. The axial absorption spectrum is shown in figure 4. The spectra are indeed identical to that of pure Rb_2CrCl_4 , substantiating the coupled spin-flip mechanism for the Mn^{2+} doped compounds.

The effect on the absorption spectrum of doping transition metal cations other than Mn^{2+} can now be considered and V^{2+} (ground state $^4A_{2g}$) and Fe^{2+} (ground state $^5B_{1g}$) were chosen. The spectrum of $\text{Rb}_2\text{Cr}_{0.97}\text{V}_{0.03}\text{Cl}_4$ is shown in figure 4b. By comparison with figure 4a, which is the same as the spectra of undoped Rb_2CrCl_4 , we see that in the V^{2+} -doped crystal there are two satellite bands between the major 6310 Å exciton-magnon bands. These satellite absorption bands, which we shall call a_1 , a_2 etc. are similar to those observed in the Mn^{2+} -doped crystals. Following a similar molecular field argument to Wood *et al* (1982) the observations may be understood by considering an isolated V^{2+} or Fe^{2+} to interact via a Heisenberg exchange mechanism, with the surrounding Cr^{2+} represented by a molecular field.

With z taken to be the spin direction in ordered Rb_2CrCl_4 then

$$\text{where } H = H_1 + H_2, \quad (11)$$

$$H_1 = -K_V S_z(\text{V}) - K_{\text{Cr}} S_z(\text{Cr}) - J_{\text{CrV}} S_z(\text{V}) \cdot S_z(\text{Cr}), \quad (12)$$

$$H_2 = J_{\text{CrV}}/2 \{S_+(\text{V})S_-(\text{Cr}) + S_-(\text{V})S_+(\text{Cr})\}, \quad (13)$$

K_m is the molecular field term around the ion M where K_V is negative and K_{Cr} is positive. J_{CrV} is the CrV exchange constant taken to be anti-ferromagnetic.

The ground state is represented as $|G\rangle = |-3/2, 2\rangle$ and the excited states are $|M'_S(\text{V}), M'_S(\text{Cr})\rangle$ where the prime notation indicates that Cr^{2+} is in its excited triplet state; a_1 is the transition to the first excited state $|-1/2, 1\rangle$, a_2 to the second excited state $|1/2, 0\rangle$ and a_3 to the third excited state $|3/2, -1\rangle$. The pure spin flip transition is to the excited state $|-3/2, -1\rangle$.

The excited state energies are given by

$$E(M'_S(\text{V}), M'_S(\text{Cr})) = -K_V M'_S(\text{V}) - K'_{\text{Cr}} M'_S(\text{Cr}) - J' M'_S(\text{V}) M'_S(\text{Cr}). \quad (14)$$

Therefore the successive energy intervals between the pure Cr, spin-flip and a_1 , a_2 , a_3 are $(-K_V - J')$, $(-K_V + K'_{\text{Cr}} - 1/2 J')$, $(-K_V + K'_{\text{Cr}} + 3/2 J')$. If $|K_V|$ is assumed to be the dominant term (i.e. $J_{\text{Cr'Cr}}$ and J_{CrV} are small) the intervals are equal as observed. To obtain more precise estimates it will be necessary to measure the spectra at lower temperatures to remove the hot bands completely (Janke *et al* 1982). Now $|K_V|$, the molecular field term around V^{2+} , is given as follows:

$$|K_V| = 2ZSJ_{\text{CrV}} = 12J_{\text{CrV}}, \quad (15)$$

Thus from figure 4b the $a_2 - a_1$ interval is 53 cm^{-1} , leading to an estimate of J_{CrV} as $\sim 4.4 \text{ cm}^{-1} \equiv 6.3 \text{ K}$ from (15). Finally the absorption bands of $\text{Rb}_2\text{Cr}_{0.95}\text{Fe}_{0.05}\text{Cl}_4$ are shown in figure 4c, measured under the same conditions. By comparison with figure 4a there are at least two satellite bands in the 623–6310 Å region. Using the same arguments as in the V^{2+} case and (15) we find J_{CrFe} is 5.2 K.

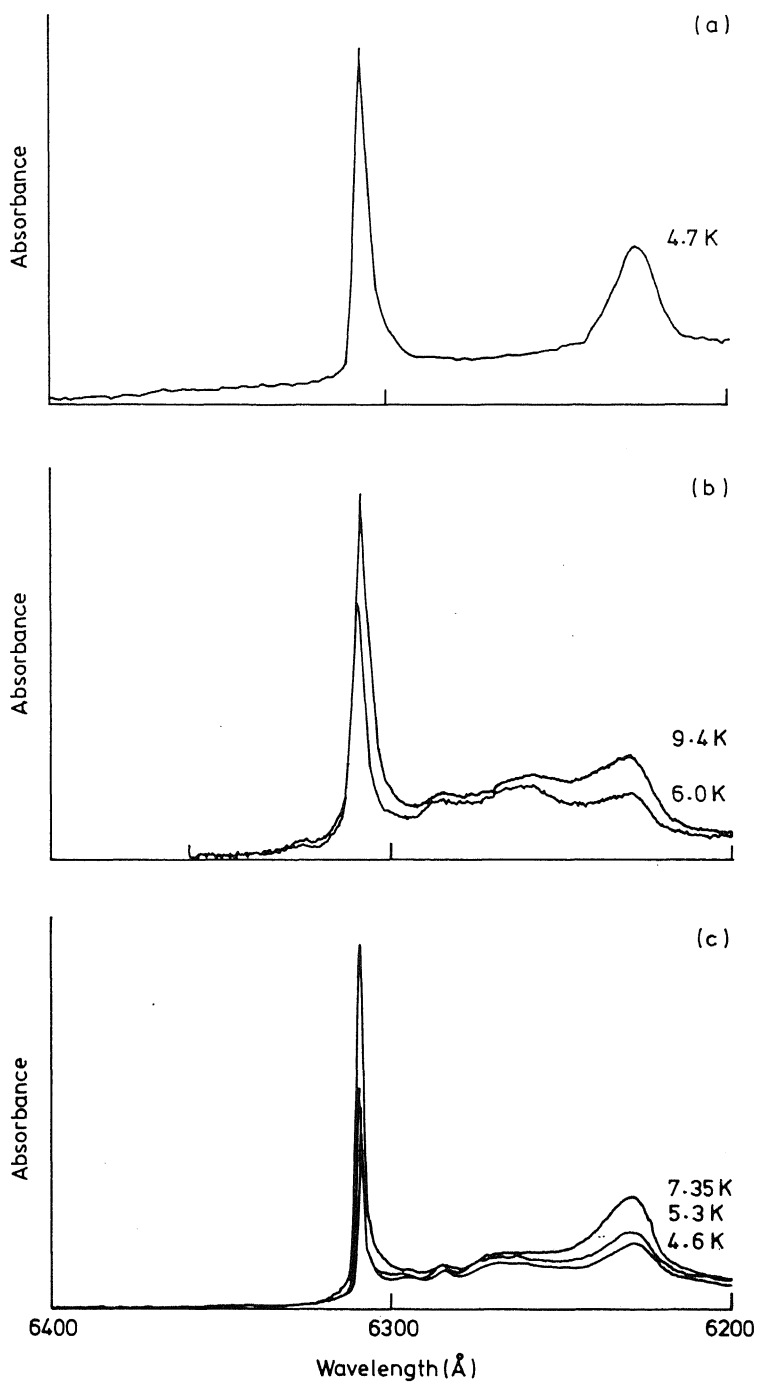


Figure 4. Axial absorption spectra of (a) $\text{Rb}_2\text{Cr}_{0.95}\text{Mg}_{0.05}\text{Cl}_4$, (b) $\text{Rb}_2\text{Cr}_{0.97}\text{V}_{0.03}\text{Cl}_4$ and (c) $\text{Rb}_2\text{Cr}_{0.95}\text{Fe}_{0.05}\text{Cl}_4$ at various temperatures.

4. Conclusions

We have shown how a combination of powder and single crystal neutron diffraction, together with optical spectroscopy, can illuminate the effect of doping either magnetic or non-magnetic cations substitutionally into the Cr^{2+} sites of the ionic ferromagnet Rb_2CrCl_4 . Powder diffraction shows that with 27% Mg^{2+} substitution long range magnetic order persists at 4.2 K and the moments remain parallel to the basal plane. From single crystal diffraction we find that substitution of 11% Mg^{2+} lowers T_c by 19% while substitution of 3% V^{2+} lowers it by 6%. By examining the satellite bands which appear alongside the exciton-magnon hot bands in the visible absorption spectrum of Rb_2CrCl_4 when it is doped with small amounts of magnetic impurities, we have also estimated near-neighbour Cr^{2+} - V^{2+} and Cr^{2+} - Fe^{2+} exchange constants. Both are antiferromagnetic in sign and respectively 6.3 K and 5.2 K in magnitude. These figures are to be compared with 3.0 K for the Cr^{2+} - Mn^{2+} exchange constant in the same material.

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EPR as a necessary complement of magnetic measurements in exchange coupled systems

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Abstract. Several examples are shown in which the complementary use of temperature dependent magnetic susceptibility measurements and EPR spectroscopy has provided information which neither technique alone could have given in the study of exchange coupled systems. For instance it is shown how EPR can help in determining the exchange pathways whose existence is observed from magnetic susceptibility measurements and more applications to monitoring weak exchange interactions determining the magnetic dimensionality, disclosing the nature of paramagnetic impurities, looking in detail into the multiplet structure of exchange coupled systems.

Keywords. EPR spectroscopy; magnetic susceptibility; exchange interactions; paramagnetic impurities; exchange coupled systems.

1. Introduction

In the study of the exchange interactions between paramagnetic centers, two techniques are most useful, namely magnetic susceptibility measurements and EPR spectroscopy. It is well-known that the information provided by them is largely complementary, the former giving an average answer from all the magnetic centers possessing different energies, while the latter can give, and in most cases it does give, the response of each individual set of centers characterized by one energy level. For instance, if we consider the case of a pair of spins $S_1 = 1/2$, $S_2 = 1$ which are strongly coupled, the total spin $S = S_1 + S_2$ is a good quantum number, yielding a quartet and a doublet. Magnetic susceptibility depends on the relative population of the two multiplets, and measuring it as a function of the temperature usually yields the energy separation between the two spin states. On the other hand EPR spectra, in the most favourable case, can show separately the doublet and the quartet, giving precious information on the details of the g tensor and of the zero field splitting tensor D , which can be obtained with difficulty through magnetic susceptibility measurements, and further on the hyperfine and superhyperfine tensors which the latter technique cannot provide. EPR is also extremely useful in monitoring weak exchange interactions, which can be obtained by magnetic susceptibility measurements only by going to extremely low temperatures, and in revealing the nature of paramagnetic impurities which can be present in the lattice. Finally using EPR it is often possible to obtain unequivocal answers on the magnetic dimensionality, which in many cases may not correspond to the structural dimensionality.

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From the above considerations one might conclude that EPR is a much stronger tool for the analysis of the magnetic coupling than the temperature dependent susceptibility measurements, but this is simply not true, since, for instance, the former can generally yield with only a low accuracy the energy separation between the thermally populated multiplets. The reason for this is that the method for determining the relative energies of the multiplets through EPR is that of measuring the signal intensities as a function of the temperature and comparing these with that of a Curie paramagnet standard. Intensity measurements in EPR are never very accurate because they are obtained by double integration of the observed signal and the possibility of overlap of different lines makes it a difficult problem even for modern spectrometers equipped with fast computers.

The conclusion of this introduction is therefore that magnetic susceptibility measurements and EPR spectroscopy are largely complementary techniques, which should always be combined in order to obtain the required knowledge of the thermally populated energy levels of exchange coupled systems. A statement like this might be conclusive, but in order not to be axiomatic, it is important to show its validity through examples, which we will take from our own experimental work on di-, tri-, tetra- and polynuclear exchange coupled systems.

In order to avoid confusion we state here that throughout this paper the exchange hamiltonians will be of the form:

$$H = \sum_{i,j} J_{ij} S_i \cdot S_j.$$

2. EPR helps in finding lost exchange pathways

We recently reported (Laugier *et al* 1986) the structure and the magnetic properties of a complex of formula $\text{CuCl}_2(\text{NITPh})_2$, where NITPh is the radical 2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxo whose formula is sketched below.

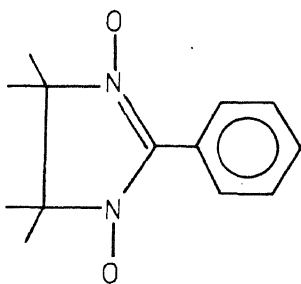


Chart 1.

The two N-O groups are completely equivalent by resonance, a result which is confirmed by the solution EPR spectra of the radical. The X-ray structure of the complex showed that two nitroxides are bound to a copper ion(II), each through one oxygen atom. The coordination of the metal ion is square planar CuO_2Cl_2 as shown in figure 1. The magnetic moment at room temperature corresponds to one unpaired electron *per* CuO_2Cl_2 unit, showing that the three spins $1/2$ are strongly coupled in an antiferromagnetic fashion to yield a ground doublet well-separated from other excited multiplets. The polycrystalline powder EPR spectra at room temperature give a g value in agreement with this view. However, on cooling, the

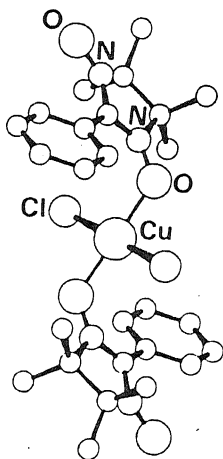


Figure 1. View of the molecular structure of dichloro-bis-(2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl) copper(II), $\text{CuCl}_2(\text{NITPHEN})_2$. (After Laugier *et al* 1986.)

magnetic susceptibility goes through a maximum at ~ 15 K, showing that some intermolecular antiferromagnetic interaction must be operative. In principle this interaction might be given by dimerization of the $\text{CuCl}_2(\text{NITPh})_2$, by a chain structure, or by three-dimensional order. The experimental points could be reasonably well-fitted with the chain model (Bonner and Fisher 1964), and not with the dimer model (Bleaney and Bowers 1952), but the problem of where the chain was remained. Looking more carefully at the structure one could find two reasonably short contacts, one between the hydrogen atom of the phenyl group of a NITPh radical with the chlorine of another CuO_2Cl_2 moiety, 284.4 pm, and another one between the N–O groups of two nitroxides belonging to two different $\text{CuCl}_2(\text{NITPh})_2$ molecules, at 394 pm. Although the latter would seem more reasonable for an effective exchange, the former could not be excluded a priori. Single crystal EPR spectra provided a definitive answer because they showed two signals corresponding to the two magnetically non-equivalent sites of the monoclinic cell. This means that the exchange pathway connects equivalent CuO_2Cl_2 moieties, therefore the H–Cl contact must be ruled out, as this is relative to a pair of magnetically non-equivalent sites in the unit cell. On the other hand the N–O contact connects $\text{CuCl}_2(\text{NITPh})_2$ molecules which are related by a translation parallel to c . This connection yields chains parallel to the c axis which are totally compatible with the EPR results.

3. EPR is sensitive to weak exchange interactions

A beautiful example of the sensitivity of EPR to weak exchange interactions is provided by the magnetic properties (Journaux *et al* 1985) of $\text{Cu}(\text{salen})\text{Ni}(\text{hfac})_2$ (salen = N,N'-ethylenebis(salicylaldiminato); hfac = hexafluoro acetyl acetonato). The crystal structure of this complex showed that it comprises the units of figure 2 and the magnetic susceptibility in the range 1–300 K was satisfactorily fit with a coupling constant $J = 23.6 \text{ cm}^{-1}$. This means that of the two states which

groups to yield a chain. The magnetic susceptibility, which shows evidence of antiferromagnetic coupling, might in principle fit the formula appropriate to isolated trinuclear species or to an alternating chain (Benelli *et al* 1984). Indeed EPR spectra revealed a hyperfine splitting due to the interaction of the unpaired electron with the copper nuclei, showing that intermolecular exchange interaction in this compound must be smaller than 0.013 cm^{-1} . No attempt was made therefore to fit the experimental magnetic data to the chain model, and indeed a satisfactory agreement was found to a trinuclear model.

Another interesting example is provided by $\text{Cu}(\text{hfac})_2(\text{TEMPOL})$, where TEMPOL is 4-hydroxy-2,2,6,6-tetramethylpiperidyl-N-oxyl, which is formed (Anderson and Kuechler 1980) by chains schematically indicated in figure 6. Again the problem is whether magnetically the compound behaves as an alternating chain, the two different coupling constants corresponding to the interaction of the nitroxide group with the closer and the farther copper ion respectively, or a two-spin model is sufficient. The EPR spectra at room temperature are clearly indicative of a triplet state (Bencini *et al* 1984), suggesting that the interaction with the farther copper ion is negligible, at least in a first approximation. Indeed magnetic susceptibility measurements down to 2 K could be interpreted with the Bleaney-Bowers approximation with a ferromagnetic J value of -13 cm^{-1} , extending (Benelli *et al* 1985) the measurements down to 40 mK a maximum in susceptibility could be observed at $\sim 80 \text{ mK}$, which was attributed to an antiferromagnetic interaction of 0.054 cm^{-1} between the nitroxide and the farther copper ion.

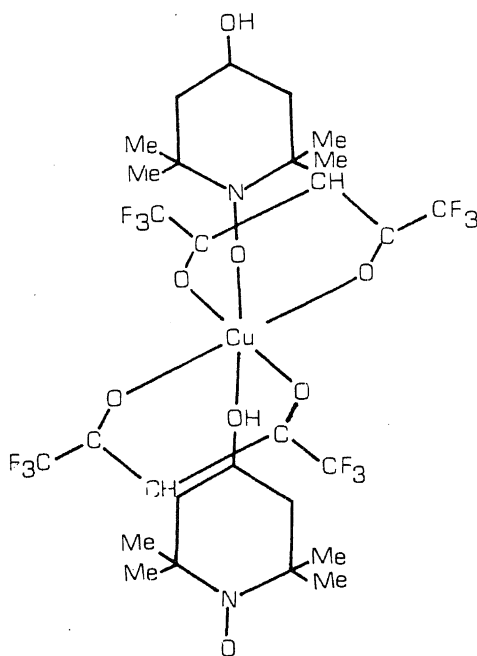


Figure 6. Sketch of the chain structure of *bis*(hexafluoroacetylacetonato)(4-hydroxy-2,2,6,6-tetramethylpiperidyl-N-oxyl)copper(II), $\text{Cu}(\text{hfac})_2\text{TEMPOL}$. (After Bencini *et al* 1984.)

5. EPR helps in revealing the nature of paramagnetic impurities

One of the most common problems encountered in the analysis of the magnetic data of antiferromagnetically coupled dimers, is that at low temperatures the magnetic susceptibility goes through a maximum and then decreases, but eventually, on further lowering the temperature, increases again. This result is usually interpreted as due to the presence of a paramagnetic impurity, which can give important effects at low temperature when the lattice becomes essentially diamagnetic.

EPR spectra can substantiate this assumption, by disclosing the nature of the impurity. A classical example is provided by copper acetate type complexes, in which the dinuclear species are antiferromagnetically (Abe and Shimada 1953) coupled. At a low temperature a spin doublet spectrum is readily observed, which must be assigned to isolated copper (II) ions. The g values of this species are identical to those of the dinuclear species, while the A values are twice as large. These results are generally justified as due to the presence of monomeric copper impurities, most probably associated with defective sites in which the second copper ion of the dimer is missing.

Recently we observed a more unusual impurity in an asymmetric dinuclear species (Bencini *et al* 1986) $[(\text{dien})\text{Cu}(\text{ox})\text{Cu}(\text{tmen})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (dien = N,N',N''-diethylene triamine; ox = oxalato; tmen = N,N,N',N'-tetramethylethylenediamine). Magnetic susceptibility measurements (Julte *et al* 1983, 1984) revealed that the inequivalent copper ions, which are bridged by an oxalato group, with an overall geometry as shown in figure 7, are antiferromagnetically coupled with a singlet-triplet separation of 75.5 cm^{-1} . Below 25 K the magnetic susceptibility increases rapidly, suggesting the presence of a paramagnetic impurity. Extending to this asymmetric dinuclear species the interpretation given for symmetric dimers above, two different kinds of "monomeric" impurities could be expected, one in which copper is in the dien environment and the other in which copper is in the tmen environment. The EPR spectra at low temperatures, however, showed the presence of a triplet species containing two equivalent copper ions. Since the spectra could be detected down to 4.2 K in this symmetric dinuclear species the two copper ions must be weakly coupled. The comparison with previous literature data (Felthouse *et al* 1977) suggested that the species responsible for the EPR spectra is $[(\text{dien})\text{Cu}(\text{ox})\text{Cu}(\text{dien})]^{2+}$.

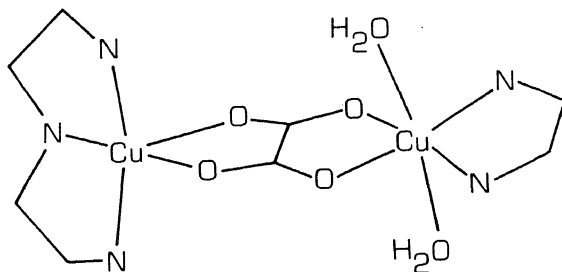


Figure 7. Overall geometry coordination in $[(\text{dien})\text{Cu}(\text{ox})\text{Cu}(\text{tmen})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (dien = N,N',N''-diethylene triamine; ox = oxalato; tmen = N,N,N',N'-tetramethylethylenediamine). (After Bencini *et al* 1986.)

From this it is apparent that in molecular lattices also there is a possibility of hosting molecules which are largely different from the building blocks of the parent lattice and that it might be desirable to investigate in more detail the nature of the "impurities" which can be formed in the normal synthetic procedure.

6. EPR looks in detail into the multiplet structure

This is the most obvious application of EPR spectroscopy, that of measuring the spectra of each individual multiplet generated by the exchange interaction which is thermally populated, in order to characterize it fully. Beyond the simple case of two $S = 1/2$ states, in the last few years many more examples have been worked out for a variable number of coupled spins of variable multiplicity (Gatteschi and Bencini 1985; Kahn 1985). It is in this field that much work remains to be done in order to understand which are the factors making the observation of the EPR spectra of some multiplets easy, and much more difficult for other ones. For instance, several Cu-Ni pairs have been characterized (Kokoszha *et al* 1967; Bencini *et al* 1980; Buluggiu 1980; Banci *et al* 1981a, b, 1982; Bencini and Gatteschi 1985; Gatteschi and Bencini 1985; Journaux *et al* 1985), which yield a quartet and a doublet, but to our knowledge, in no case have both been characterized in the same compound by EPR spectroscopy. Indeed, in general the doublet spectra are rather easily observed, but the spectra in the quartet state has to our knowledge been reported only in one case in which the coupling is ferromagnetic (Bencini *et al* 1980). Probably it is relaxation factors which are dominant: for an antiferromagnetic couple the lines of the quartet at high temperatures are broad, and at low temperatures, where presumably relaxation might be slow enough, the quartet is depopulated.

More interesting results could be obtained in the case of copper-manganese pairs where the spectra of both the $S = 2$ and $S = 3$ states were observed. $\text{Cu}(\text{prp})_2\text{enMn}(\text{hfac})_2$ (Hall *et al* 1981), where $(\text{prp})_2\text{en}$ is the Schiff base formed by 2-hydroxypropionophenone and ethylenediamine, hfac is hexafluoroacetyl-acetonato, contains dinuclear species (O'Connor *et al* 1979) in which the copper(II) ion is in a square planar environment and manganese(II) is octahedral, as shown in figure 8. Magnetic susceptibility measurements showed that the $S = 2$ state lies 78 cm^{-1} lower than the $S = 3$ state. EPR spectra showed (Banci *et al* 1981c) that the g values of the two multiplets are different, as expected (Gatteschi and Bencini 1985), and also that the zero-field splitting tensors differ. This result should also be kept in mind for the interpretation of the magnetic data, allowing for different g values in the various multiplets.

Things become more complicated for three- and tetranuclear species, where the number of thermally populated states increases. EPR spectra of both the ground $S = 3/2$ and of an excited $S = 5/2$ state were observed for $\text{Mn}(\text{hfac})_2(\text{TEMPO})_2$ and $\text{Mn}(\text{hfac})_2(\text{PROXYL})_2$ ($\text{TEMPO} = 2,2,6,6\text{-tetramethyl piperidinil-N-oxy}$; $\text{PROXYL} = 2,2,5,5\text{-tetramethylpyrrolidinil-1-oxy}$) (Benelli *et al* 1986a). In these complexes the metal ion ($S = 5/2$) is octahedrally coordinated to two nitroxides and two hexafluoroacetylacetonate ions (Dickman *et al* 1986). The coupling was found by magnetic susceptibility measurements to be antiferromagnetic, $J = 158\text{ cm}^{-1}$ and $J = 210\text{ cm}^{-1}$ for the TEMPO and PROXYL derivative

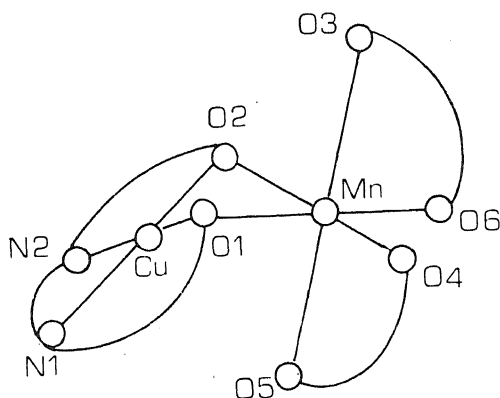


Figure 8. Sketch of the $\text{Cu}(\text{prp})_2\text{enMn}(\text{hfac})_2$ complex ((prp)₂en = Schiff base formed by 2-hydroxypropiophenone and ethylenediamine, hfac = hexafluoroacetylacetonato). (After Banci *et al* 1981c.)

respectively. The possible total spin states are $S = 3/2, 5/2, 5/2$ and $7/2$ and the EPR spectra helped in confirming the order of the two different sextuplet states. Indeed the spin hamiltonian parameters of the different multiplets are different and an analysis of the zero field splitting tensors allowed us to identify the $S = 5/2$ of which we observed the EPR spectra.

It is perhaps useful to mention here that although we have studied the EPR spectra of several trinuclear species containing three $S = 1/2$ spins we never observed (Banci *et al* 1983a, b; Bencini *et al* 1985a; Benelli *et al* 1986b; Gatteschi *et al* 1987) the spectra of the quartet and of the two doublets which are generated by the exchange interactions, and generally only one averaged signal is observed. The reason for this is not clear, although intermolecular exchange can be considered to be important.

7. Conclusions

We hope to have shown the many different kinds of information that can be obtained from the analysis of the EPR spectra of exchange coupled systems. Due to the limit of space we had to confine the treatment to our own work, but many more might be found in the literature. Perhaps the most important examples might be those relative to one- and two- dimensional magnets, where the analysis of the EPR spectra yielded unvaluable information on the spin dynamics (Drumheller 1982). Also in the study of biological compounds, in which a magnetic coupling is present, EPR spectra have been of fundamental importance for recognizing the nature of the centers (Palmer 1983; Solomon and Wilcox 1985; Bencini *et al* 1985b, c). We feel that this technique, which is now slightly older (Zavoisky 1945) than forty years, is still young and vital, and has still many important results to provide.

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Magnetic properties and molecular structure of cobalt(II) oxydiacetate trihydrate

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Abstract. The crystal and molecular structure of cobalt(II) oxydiacetate trihydrate, $\text{Co}(\text{C}_2\text{H}_3\text{O}_5) \cdot 3\text{H}_2\text{O}$, has been determined from single-crystal, three-dimensional x-ray diffraction counter data. The compound crystallizes as dark red violet platelets in space group $P2_1/n$ of the monoclinic system with $Z = 4$ and having cell dimensions $a = 7.128(1)\text{\AA}$, $b = 10.384(2)\text{\AA}$, $c = 11.122(1)\text{\AA}$, and $\beta = 91.51(1)^\circ$. The structure was refined to $R = 0.042$ and $R_w = 0.053$. The cobalt(II) ion has a distorted octahedral coordination in which the oxydiacetate acts as a tridentate chelate and the three remaining coordination sites are occupied by two water molecules and an oxygen atom from a carboxylate group of an adjacent oxydiacetate dianion. This latter linkage forms a chain structure. The chains are packed in layers and there is extensive hydrogen bonding between the layers. The magnetic susceptibility of cobalt(II) oxydiacetate trihydrate is dependent on the applied magnetic field. In an applied magnetic field of 1,000 Oe, the maximum susceptibility occurs at 2.51 K, and the inflection point below T_{max} lies at 2.40 K. (χ_{max} , T_{max}) at 100 Oe and 10,000 Oe are (0.257 emu/mole, 2.63 K) and (0.227, 1.76 K).

Keywords. Molecular structure; cobalt(II) oxydiacetate trihydrate; magnetic susceptibility; cobalt(II) chain compound; three-dimensional magnetic ordering.

1. Introduction

The study of low-dimensional magnetic materials continues to attract attention, since these substances may provide real examples for the various theoretical models of magnetic behavior (de Jongh and Miedema 1974), or may be candidates for materials with prescribed properties. For example, there are few molecular based, chelated coordination compounds that exhibit cooperative ferromagnetic behavior. From previous work in our laboratory, the layered compound copper(II) oxydiacetate hemihydrate (Corvan *et al* 1980) was identified as being an insulating ferromagnet with $T_C = 3.3\text{ K}$, an intralayer exchange coupling constant of $+4.66\text{ cm}^{-1}$, and an out-of-plane anisotropy field of 250 Oe. The results of this work have stimulated the synthesis and characterization of other transition metal oxydiacetate salts. The molecular structure and magnetic properties of cobalt(II) oxydiacetate trihydrate are discussed in this article.

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2. Experimental

2.1 Synthesis

Samples of cobalt(II) oxydiacetate trihydrate were prepared by a modification of the procedure described earlier (Whitlow and Davey 1975). Excess oxydiacetic acid (diglycolic acid, obtained from the Aldrich Chemical Co.) was added to cobalt(II) carbonate, and the resultant deep red violet crystals were recrystallized from water to give irregular platelets. Analysis (Galbraith Laboratories, Inc., Knoxville, TN, USA). Calculated for $[\text{Co}\{\text{O}(\text{CH}_2\text{CO}_2)_2\}]\cdot 3\text{H}_2\text{O}$: C 19.61; H 4.11. Found: C 19.54; H 3.97.

2.2 Magnetic measurements

Magnetic susceptibility data were collected using a Princeton Applied Research Model 155 Foner-type (Foner 1959) vibrating sample magnetometer (VSM) using procedures that have been described earlier (Corvan *et al* 1980). The magnetometer was calibrated with $\text{HgCo}(\text{NCS})_4$ (Figgis and Nyholm 1958; Brown *et al* 1977). Samples of the standard and compounds under study were contained in precision milled Lucite sample holders. Approximately 150 mg of each were used. Diamagnetic corrections for the constituent atoms were made by using Pascal's constants, and corrections for temperature independent paramagnetism were estimated from tabulated data (Figgis *et al* 1960; König 1966; Weller *et al* 1979).

2.3 X-ray crystallography

Red violet colored crystals of the complex were grown by slow evaporation of a concentrated aqueous solution. All the larger crystals examined by Weissenberg and precession photographs turned out to be twinned. An untwinned monoclinic prism of dimensions $(0.30 \times 0.15 \times 0.10)$ mm was selected and used for data collection on an Enraf Nonius CAD4 diffractometer using a molybdenum tube and a graphite monochromator. The unit cell constants were obtained by a least-squares refinement of the setting angles of 25 reflections with $\theta \geq 30^\circ$. The intensity data were collected at $20 \pm 2^\circ\text{C}$ by the variable speed $\omega - 2\theta$ scan in the range $2^\circ \leq 2\theta \leq 55^\circ$. The scan range in ω for each peak was calculated from the formula $S = M_s + W_s \tan \theta$, where M_s is estimated from the mosaic spread of the crystal, and W_s allows for increasing peak width with θ due to wavelength dispersion. M_s and W_s were given values of 1.00 and 0.35, respectively. Scan ranges were extended by 25% on each side of a peak for the moving-background measurement. The total time spent on the two backgrounds was one-half of that spent on the peak. The intensities of three standard reflections monitored every three hours showed no significant variation thus assuring the stability of the crystal in the X-ray beam. The intensities were corrected for background and Lorentz and polarization factors with a locally written program based on a method described earlier (Corefield *et al* 1967), but the data were not corrected for absorption ($\mu = 21.0 \text{ cm}^{-1}$).

The structure was solved by the conventional heavy atom and difference Fourier techniques, and refined by the full-matrix least-squares method to the conventional residuals R and R_w of 0.042 and 0.053, respectively, where R and R_w are defined as

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, \text{ and}$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}.$$

The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. The anomalous dispersion factors, $\Delta f'$, and $\Delta f''$, for Co and Cl (International Tables for X-ray Crystallography 1974), were included in the calculations of F_c . The atomic scattering factors for hydrogen were taken from a standard source (Stewart *et al* 1965). All the non-hydrogen atoms were refined with anisotropic thermal vibration parameters and the hydrogen atoms with isotropic thermal vibration parameters. The two hydrogen atoms belonging to one of the water molecules could not be located from the difference Fourier. The largest peak in the final difference Fourier had a height of 0.4 e⁻. The crystal data are collected in table 1.

The positional parameters with their estimated standard deviations are given in table 2. Tables of structure amplitudes and thermal parameters are deposited as supplementary material.

Table 1. Crystal data.

Co(C ₄ H ₄ O ₅)·3H ₂ O	MW = 245.1
$a = 7.128(1)\text{\AA}$	$D_c = 1.98\text{ g cm}^{-3}$
$b = 10.384(2)$	$Z = 4$
$c = 11.122(1)$	$\lambda(\text{Mo-K}\alpha_1) = 0.70926\text{ \AA}$
$\beta = 91.51(1)^\circ$	$\mu(\text{Mo-K}\alpha) = 21.0\text{ cm}^{-1}$
$U = 822.93\text{ \AA}^3$	NO = 1549 $\geq 3\sigma(\text{I})$
Monoclinic, $P2_1/n$	$R = 0.042$, $R_w = 0.053$

Table 2. Positional parameters with their estimated standard deviations.

Atom	x/a	y/b	z/c
Co	0.0719 (1)	0.3927 (1)	0.3032 (1)
Q (1)	0.2949 (5)	0.2822 (3)	0.2373 (3)
C (1)	0.2773 (7)	0.1618 (5)	0.2354 (4)
O (2)	0.4018 (5)	0.0872 (3)	0.1961 (3)
C (2)	0.0996 (8)	0.1005 (5)	0.2807 (6)
O (3)	-0.0179 (5)	0.2031 (3)	0.3165 (4)
C (3)	-0.1927 (7)	0.1734 (5)	0.3675 (6)
C (4)	-0.2737 (7)	0.2993 (5)	0.4148 (5)
O (4)	-0.4168 (5)	0.2921 (4)	0.4740 (3)
O (5)	-0.1880 (5)	0.4036 (3)	0.3883 (3)
OW (1)	0.2284 (6)	0.3881 (4)	0.4687 (4)
OW (2)	-0.0342 (5)	0.4045 (4)	0.1263 (3)
H1C (2)	0.138 (8)	0.042 (6)	0.353 (5)
H2C (2)	0.035 (9)	0.035 (7)	0.198 (6)
H1C (3)	-0.085 (8)	0.140 (5)	0.304 (5)
H2C (3)	-0.163 (9)	0.103 (7)	0.449 (6)
H1OW (1)	0.082 (12)	0.368 (8)	0.465 (7)
H2OW (1)	0.231 (10)	0.446 (7)	0.499 (6)
H1OW (3)	0.640 (9)	0.258 (7)	0.059 (6)
H2OW (3)	0.532 (11)	0.327 (9)	0.110 (9)

3. Results and Discussion

3.1 Molecular and crystal structure

The cobalt(II) ion has a distorted octahedral coordination in which the oxydiacetate anion acts as a tridentate chelate the three chelating atoms being the ether oxygen O(3) and an oxygen from each of the two carboxylate groups. The remaining three coordinating sites are occupied by two water molecules, and, as shown in the ORTEP (Johnson 1976) drawing of the structure, an oxygen atom from a carboxylate group of another oxydiacetate anion (figure 1). All Co—O bond distances (table 3) lie within a narrow range, the shortest being 2.028(3) Å and the longest 2.128(4) Å. Due to the constraints imposed by the oxydiacetate chelate the bond angles around the cobalt atom vary considerably from the ideal values of 90° or 180° expected for an octahedral coordination. Thus, the bond angles subtended at Co by the three pairs of *trans* oxygen atoms, i.e., the angles O(1)—Co—O(5), O(3)—Co—O(2ⁱ), and OW(1)—Co—OW(2) are 150.0°, 166.5°, and 169.4°, respectively, while the six O—Co—O bond angles subtended by the *cis* oxygen atoms range from a low of 75.3° to a high of 118.2° (table 3).

The oxydiacetate ligand is approximately planar with the cobalt atom lying approximately in the plane (table 4). It is apparent from the deviations of atoms from the mean plane that the two halves of the ligand are slightly folded about the

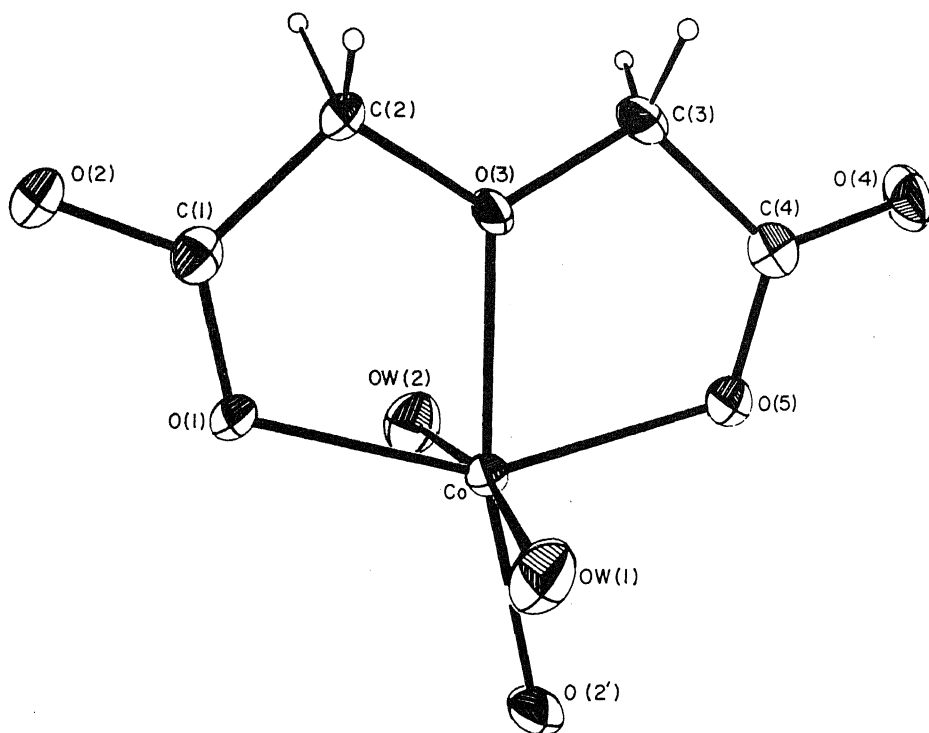


Figure 1. An ORTEP view of the complex with 40% probability of thermal ellipsoids for non-hydrogen atoms, and spheres of arbitrary size for hydrogen atoms. OW(1) and OW(2) are coordinated water molecules whose hydrogen atoms are not shown.

Table 3. Bond distances and bond angles with estimated standard deviations in parentheses.

<i>Bond distances (Å)</i>			
Co—O (1)	2.108 (3)	C(1)—O (2)	1.265 (6)
Co—O (3)	2.077 (4)	C(1)—C (2)	1.516 (7)
Co—O (5)	2.106 (3)	C(2)—O (3)	1.418 (6)
Co—O (2')	2.028 (3)	C(3)—O (3)	1.417 (6)
Co—OW (1)	2.128 (4)	C(3)—C (4)	1.528 (7)
Co—OW (2)	2.092 (4)	C(4)—O (4)	1.231 (6)
C(1)—O (1)	1.257 (6)	C(4)—O (5)	1.282 (6)
<i>Bond angles (°)</i>			
O(1)—Co—O (3)	75.3 (1)	OW(1)—Co—OW (2)	169.4 (2)
O(1)—Co—O (5)	150.0 (1)	Co—O(1)—C (1)	118.1 (4)
O(1)—Co—O (2')	118.2 (1)	O(1)—C(1)—C (2)	119.8 (5)
O(1)—Co—OW (1)	84.6 (2)	O(1)—C(1)—O (2)	123.5 (5)
O(1)—Co—OW (2)	87.8 (2)	O(2)—C(1)—C (2)	117.2 (5)
O(3)—Co—O (5)	75.1 (1)	C(2)—C(2)—O (3)	106.4 (4)
O(3)—Co—O (2')	166.5 (2)	C(2)—O(3)—C (3)	118.7 (4)
O(3)—Co—OW (1)	94.2 (2)	C(2)—O(3)—Co	120.5 (4)
O(3)—Co—OW (2)	91.0 (2)	C(3)—O(3)—Co	120.7 (4)
O(5)—Co—O (2')	91.5 (1)	O(3)—C(3)—C (4)	107.2 (4)
O(5)—Co—OW (1)	93.4 (2)	C(3)—C(4)—O (5)	117.2 (4)
O(5)—Co—OW (2)	96.8 (2)	C(3)—C(4)—O (4)	117.3 (5)
O(2')—Co—OW (1)	88.4 (2)	O(4)—C(4)—O (5)	125.5 (5)
O(2')—Co—OW (2)	88.6 (2)	C(4)—O(5)—Co	119.2 (4)

O(2') refers to atom O(2) in symmetry position ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$).

Table 4. Deviations in Å of atoms from the mean least-squares plane through designated atoms.

Co (06), O (1) (-0.03), C (1) (-0.04), C (2) (-0.01), O (3), O (3) (0.06) C (3) (0.05), C (4) (-0.09), O (5) (-0.01), O (2') (0.11),* O (2) (-0.07),* O (3) (-0.26),* OW (1) (-2.07),* OW (2) (2.14),* OW (3) (0.51)
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* Atoms not included in the mean plane calculation.

Co—O(3) bond. The bond distances and angles in the ligand are similar to those reported for the free ligand (Davy *et al* 1973) and for copper(II)-oxydiacetate hemihydrate (Whitlow *et al* 1975).

There are some noteworthy differences in the coordination geometry around the metal ion between the Co(II) complex reported here and copper(II)oxydiacetate hemihydrate. In the Co(II) complex the metal to ether oxygen distance is quite normal (2.077 Å) whereas in the Cu(II) complex it is quite long (2.488 Å). This has the effect of making the terminal chelating oxygens O(1) and O(5) *trans* to each other in the former and *cis* in the latter. Only one of the remaining two oxygen atoms of the ligand, i.e., O(2), is coordinated in the Co(II) complex whereas both O(2) and O(4) are coordinated in the Cu(II) complex.

The crystal structure consists of infinite chains of Co(II)oxydiacetate units covalently linked to each other through Co—O(2') bonds, where O(2') belongs to an adjacent ligand. The chain direction is delineated in figure 2 by showing the corresponding bonds as full dark lines. The chains are packed in layers. There is

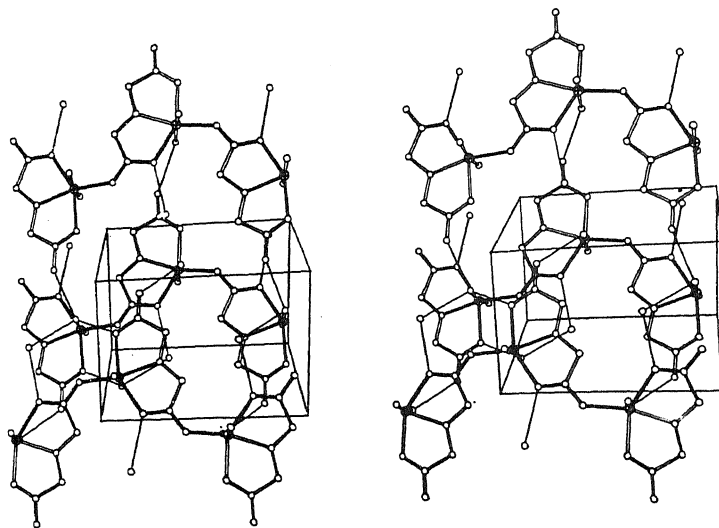


Figure 2. A stereoscopic view of the structure with the layers slightly tilted to show *trans*-coordinated water molecules. Superexchange pathways are shown with full bonds and hydrogen bonds as thin lines.

intra- as well as interlayer interaction through hydrogen bond formation with water molecules, with the three dimensional structure resulting from hydrogen bonding between the layers.

3.2 Magnetic properties

Magnetic studies of low-dimensional cobalt(II) compounds are of especial interest in view of the expected anisotropic nature of the exchange interactions as implied by the exchange Hamiltonian

$$H = -2J \sum_{i \leq j}^N \alpha \hat{S}_i^z \hat{S}_j^z + \beta \hat{S}_i^x \hat{S}_j^x + \gamma \hat{S}_i^y \hat{S}_j^y.$$

Diverse properties may be anticipated. Frequently, cobalt(II) chain compounds have Ising-like behavior ($\beta = \gamma = 0$), although XY behavior has been identified ($\alpha = 0$), and Heisenberg theory has been applied in certain cases. Both ferromagnetic ($+J$) and antiferromagnetic ($-J$) exchange coupling are known. Single ion anisotropy, g value anisotropy, and antisymmetric exchange interactions may result in spin canting, and metamagnetic materials are known (see Hatfield *et al* 1982).

The cobalt(II) single ion has an electronic configuration of d^7 , and the ground state is $^4T_{1g}$ in an octahedral environment. The degeneracy is lifted by low symmetry crystal field components and spin-orbit coupling (for the free ion $\lambda = -180 \text{ cm}^{-1}$) yielding six doublets. In some circumstances, such as the present in cobalt oxydiacetate trihydrate, the lowest lying doublet has $S' = 1/2$. In an octahedral environment, the g tensor is isotropic and has the value 4.33, but in lower symmetry environments the g tensor becomes very anisotropic. The three principal values sum to 13 in first order in the limit of a weak crystal field (Abragam *et al* 1951; Bleaney *et al* 1951), but experimentally observed g tensors

show a wide range of values (see Orton 1968). In addition to the orbital contributions, there are contributions to g from exchange interactions with the contributions being proportional to the sum of the exchange integrals from all of the neighbors (Hutchings *et al* 1963). For example, an excellent fit of the magnetic susceptibility data for $\text{Co}(\text{pyridine})_2\text{Cl}_2$, an Ising chain with ferromagnetic interactions, was obtained by using $g_{\parallel} = 7.0$ and $g_{\perp} = 5.0$ (Pires *et al* 1978).

The magnetic properties of cobalt oxydiacetate trihydrate are dependent on the applied magnetic field. Data collected in the temperature range 35 to 110 K in an applied magnetic field of 10,000 Oe may be fit by the Curie Weiss law by using a Simplex nonlinear least-squares fitting program (Spendley *et al* 1962; Nelder *et al* 1965; O'Neill 1971) with the parameters $C = 2.684$ and $\theta = -26.9^\circ$ while data collected in the same temperature range in an applied magnetic field of 1,000 Oe may be fit with the parameters $C = 2.806$ and $\theta = -24.1^\circ$. The data collected in an applied magnetic field of 1,000 Oe are displayed in figure 3 where it may be seen that the magnetic susceptibility reaches a maximum value at 2.5 K, and that there is an abrupt decrease at lower temperatures. The temperature at which an inflection occurs is at 2.40 K, and this may be tentatively identified as the critical temperature of a canted antiferromagnet, since the maximum value of the magnetic suscepti-

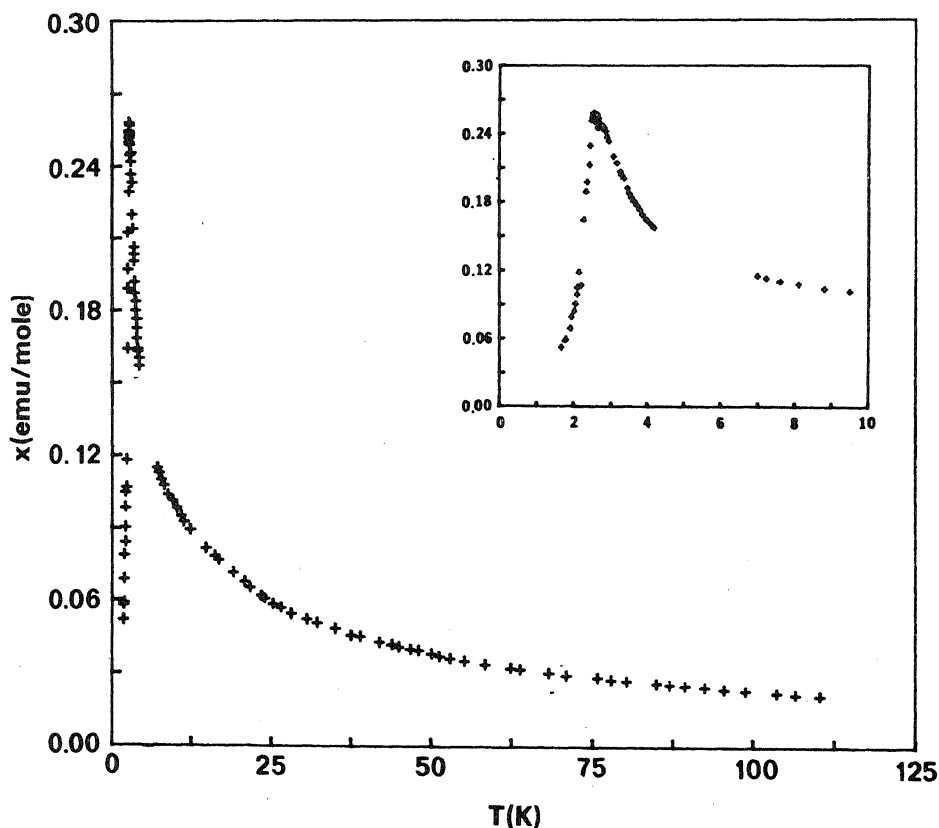


Figure 3. Magnetic susceptibility data for cobalt oxydiacetate collected in an applied field of 1,000 Oe. The low temperature data are shown in the inset with an expanded temperature scale.

bility is too low for ferromagnetic interactions. The transition seen in the 1,000 Oe magnetic data is suppressed at 10,000 Oe, and, thus, T_C must lie below the low temperature of the measurements, that being 1.8 K. Magnetic data were collected in an applied magnetic field of 100 Oe in the temperature range 1.9–30 K. Owing to a poor signal to noise ratio, it was not possible to obtain magnetic susceptibility data above 30 K in the low applied magnetic field of 100 Oe by using the vibrating sample magnetometer, and, thus, data for a Curie-Weiss law were not obtained. At 100 K, $(\chi_{\max}, T_{\max})$ are (0.257 emu/mole, 2.63 K), and the inflection occurs at 2.47 K.

The parameters from the Curie-Weiss fits have limited meaning, but they do lead to the conclusion that the ground state is a doublet with the $|\pm 3/2\rangle$ state lying at much higher energies. With this fact in mind, the magnetic data were analyzed using the Ising theory for $S = 1/2$ (Bonner *et al* 1964, Pires *et al* 1978). The appropriate equations are

$$\chi_{\perp} = [Ng_{\perp}^2 \mu_B^2 / 4 |J|] [\tanh(\beta |J|/2) + (\beta |J|/2) \operatorname{sech}^2(\beta |J|/2)]$$

$$\chi_{\parallel} = N\beta [g_{\parallel}^2 \mu_B^2 / 4] [\exp(\beta J) / \{1 + (\beta/\beta_C) \exp\{(\beta - \beta_C)J\}\}]$$

where $\beta = 1/kT$ and $\beta_C = 1/kT_C$. These equations were fitted to the experimental data collected with an applied field of 1000 Oe using a Simplex routine. The best-fit parameters are collected in table 5. The high temperature limit of the data used in the fitting calculations was taken to be 80 K in order to avoid population of the $|\pm 3/2\rangle$ state, and a low temperature limit of 3.8 K was selected in order to avoid pretransitional effects. However, the fit was not very good between 9–10 K. In the temperature range 3.8 to 9–10 K the calculated magnetic susceptibilities deviate as much as 10% from the observed data. As temperature approached, the paramagnetic susceptibility rises more rapidly than predicted by the Ising chain model, and this may be a consequence of the onset of ferromagnetism. Such weak ferromagnetism could arise from antisymmetric exchange (Dzyaloshinsky 1958; Moriya 1963) of the form

$$D_{ij} \cdot [S_i \times S_j]$$

which results in a canting of the spins. It is apparent from figure 2 that adjacent cobalt(II) ions in the chain are not related by a center of symmetry, and, thus, antisymmetric exchange interactions are allowed.

The available magnetic data show that cobalt(II) oxydiacetate trihydrate is an excellent candidate for the study of changes to higher dimensionality in an anisotropic spin system. In view of the extensive hydrogen bonding network between chains and layers, it is anticipated that changes in the dimensionality will be reflected in the magnetic properties of single crystals. Unfortunately, all

Table 5. Magnetic data for cobalt oxydiacetate trihydrate.

Applied field (Oe)	$T_{\max}$ (K)	T_C (K)	J (cm ⁻¹)	$g_{\parallel}$	$g_{\perp}$
10,000	1.7	< 1.7			
1,000	2.51	2.40	-4.0	8.27	2.93
100	2.63	2.47			

crystals examined to date have been twinned, and measurements on crystals in near-zero applied magnetic fields must await the growth of appropriate crystals for the measurements.

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Irregular spin state structures in heteropolymetallic systems

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Abstract. In an *ABA* symmetric and linear trinuclear system where the interaction between terminal ions is assumed to be negligible, the distribution in energy of the spin states depends on the relative values of the spins S_A and S_B . If $2S_A \leq S_B$, the spin state structure is regular in the sense where the spin multiplicity varies monotonically with the energy; if $2S_A > S_B$, it is irregular. A Cu(II)Ni(II)Cu(II) triad illustrates the former situation and a Mn(II)Cu(II)Mn(II) the latter. The concept of irregular spin state structure may be extended to the ordered bimetallic chains $(AB)_N$ with $N \rightarrow \infty$. The main theoretical ideas concerning these systems are presented as well as some typical examples. In particular, it is shown that a Cu(II)Mn(II) chain with an antiferromagnetic interaction between nearest neighbors exhibits a ferromagnetic-like behavior in the low temperature range. This corresponds to one-dimensional ferrimagnetism. Finally, it is emphasized that this concept of irregular spin state structure might lead to the first genuine molecular ferromagnets.

Keywords. Polymetallic complexes; one-dimensional compounds; ferrimagnetism; ferromagnetism; molecular ferromagnets.

1. Introduction

Since the pioneering work of Bleany and Bowers (1952), a very large number of papers have been devoted to binuclear systems where two identical magnetic metal ions interact within the molecular unit (Willett *et al* 1985). By far, the most highly documented are the copper(II) complexes. In contrast, relatively few investigations so far have dealt with heteropolymetallic systems with more than two interacting centers. This paper is devoted to this problem, or more exactly, to a part of this problem. Our main goal is to introduce the concept of irregular spin state structure and to stress that the design and the study of heteropolymetallic systems with irregular spin state structures open quite new perspectives in the field of molecular magnetism as well as in that of molecular materials.

This paper is organized as follows: In §2, we define the concept of spin state structure in a polymetallic compound and we point out that the spin state structure of a trinuclear species may be regular or irregular. An example of each situation is then presented. Section 3 is devoted to a very important new class of magnetic systems, namely, the ordered bimetallic chains. In §4, finally, we briefly point out that the concept of irregular spin state structure might lead to the first genuine molecular ferromagnets.

2. Regular and irregular spin state structures in trinuclear systems

In this section, we propose to introduce the concept of regularity and irregularity in the spin state structure. This concept has already led to the synthesis of polymetallic

systems in which the ground state has a very high spin multiplicity. It might be a key for the design of molecular ferromagnets, as we shall see in §4.

2.1 Concept of spin state structure

Let us consider a symmetric and linear trinuclear system ABA where the interacting centers have no orbital degeneracy and let us assume that the interaction between terminal centers is negligible with regard to the interaction between nearest neighbors. The Hamiltonian suitable for determining the spin states is:

$$H = -J(\hat{S}_{A1} \cdot \hat{S}_B + \hat{S}_{A2} \cdot \hat{S}_B), \quad (1)$$

where the interactions are assumed to be purely isotropic. Several situations can be encountered concerning the distribution in energy of the spin states, according to the relative values of S_A and S_B . More precisely, three cases have to be distinguished: (i) if $2S_A \leq S_B$, we have a *regular spin state structure*, in the sense where the spin multiplicity varies monotonically with the energy. If the interaction is antiferromagnetic, the ground state has the lowest spin multiplicity and the most excited state the highest spin multiplicity, the situation being reversed for a ferromagnetic interaction. As for the magnetic behavior arising from the regular spin state structure, it is such that upon cooling down, $\chi_M T$ continuously decreases, then finally reaches a plateau corresponding to the temperature range where only the $S = S_B - 2S_A$ ground state is populated for $J < 0$, and continuously increases up to a plateau corresponding to the temperature range where only the $S = S_B + 2S_A$ ground state is populated for $J > 0$. The $\text{Cu(II)Ni(II)Cu(II)}$ complex of §2.2 provides an example of antiferromagnetic interaction in a trinuclear system with regular spin state structure. As additional example, we give the spin state structure for an antiferromagnetically coupled ABA triad with $S_A = 1$ and $S_B = 5/2$ in figure 1. S regularly increases from $S = 1/2$ for the ground state to $S = 9/2$ for the most excited state; (ii) If $2S_A = S_B + 1/2$ with S_A and $S_B \neq 1/2$, the spin state structure becomes irregular; the spin multiplicity does not vary

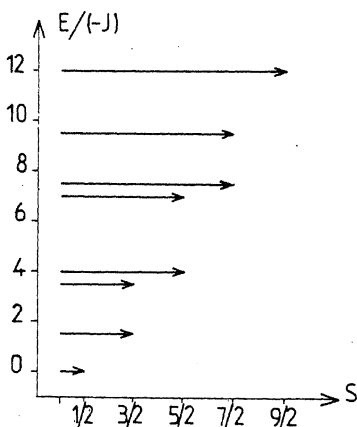


Figure 1. Spin state structure for a symmetric ABA triad with $S_A = 1$ and $S_B = 5/2$.

monotonically with energy anymore. Nevertheless, for $J < 0$, the ground state is a doublet and retains the lowest spin multiplicity; $\chi_M T$ continuously decreases upon cooling down. An example of such an intermediate case is provided by the ABA triad with $S_A = 3/2$ and $S_B = 5/2$. Its spin state structure is shown in figure 2. For $J < 0$, the ground state is a doublet and the first excited state a quartet but the second excited state is again a doublet etc . . . ; (iii) if $2 S_A > S_B + 1/2$, the spin state structure is even more irregular and for $J < 0$, the $S_g = 2 S_A - S_B$ ground state is not that of lowest spin multiplicity. On the other hand, the most excited state is always that with the largest $S (= 2 S_A + S_B)$. This may have quite an important consequence as far as the magnetic behavior is concerned. At very high temperature, when $kT > |J|$, $\chi_M T$ is constant with a value corresponding to what is expected for non coupled $2 A + B$ centers. When H begins to cool down, the first state to be thermally depopulated is that of highest spin multiplicity, so that $\chi_M T$ decreases. In the low temperature range now, when only a few excited states are populated, upon cooling down, one depopulates states with $S > S_g$ and $\chi_M T$ may increase. Therefore, $\chi_M T$ exhibits a minimum at a non zero temperature. To our knowledge, this situation has been reported for the first time, without being discussed, by Ginsberg *et al* (1968) for nickel(II) trimers. It must be emphasized here that this increase of $\chi_M T$, upon cooling below the temperature of the minimum, occurs although the interaction is antiferromagnetic. In this low temperature range, the magnetic behavior is reminiscent of what happens for a ferromagnetically coupled system. The larger $2 S_A$ with regard to S_B , the more irregular the spin state structure. Particularly interesting in this respect is the ABA triad with $S_A = 5/2$ and $S_B = 1/2$. Its spin state structure is depicted in figure 3. For $J < 0$, going down in energy, S first decreases from $11/2$ to $1/2$ then increases from $1/2$ to $9/2$. It follows that a very pronounced increase of the $\chi_M T$ versus T plot may be expected in the low temperature range. An example of this kind is given in §2.3.

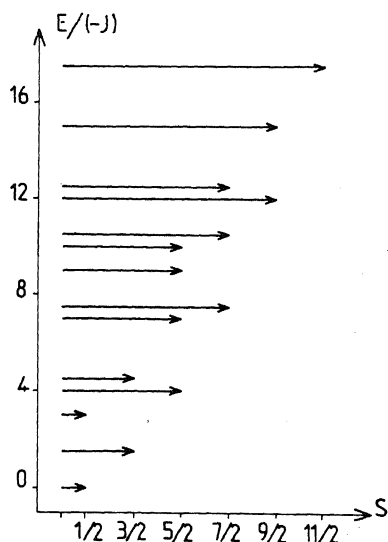


Figure 2. Spin state structure for a symmetric ABA triad with $S_A = 3/2$ and $S_B = 5/2$.

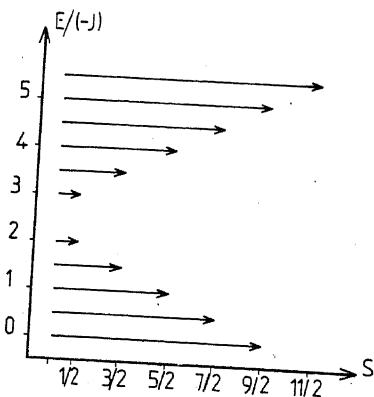


Figure 3. Spin state structure for a symmetric *ABA* triad with $S_A = 5/2$ and $S_B = 1/2$.

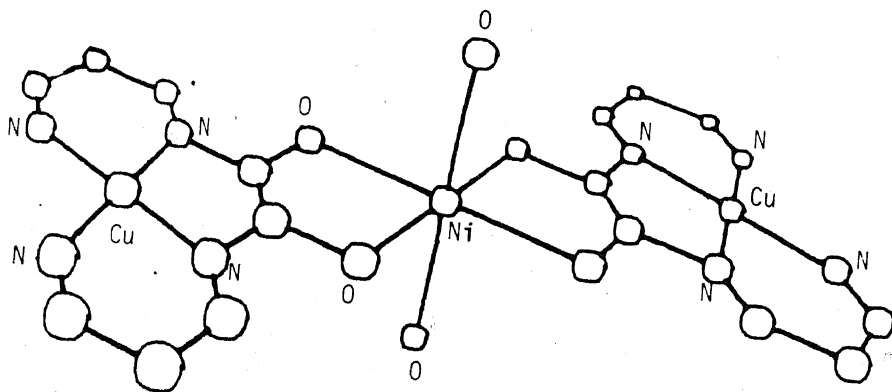


Figure 4. Structure of $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2]^{2+}$.

2.2 $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$

The condensation of two moles of $\text{Cu}(\text{oxpn})$ with one mole of $\text{Ni}(\text{II})$ perchlorate affords $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$. (oxpn) is *N, N'*-bispropylene-diamine-oxamido (Journaux *et al* 1986). The structure of the trinuclear cation with the $\text{Cu}(\text{II})\text{Ni}(\text{II})\text{Cu}(\text{II})$ triad is schematized in figure 4.

The spin Hamiltonian in zero field for this compound is written as:

$$H = -J(\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Ni}} + \hat{S}_{\text{Cu2}} \cdot \hat{S}_{\text{Ni}}) - j\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Cu2}}, \quad (2)$$

and the relative energies $E(S, S')$ of the low lying states are:

$$\begin{aligned} E(0, 1) &= 0, \\ E(1, 1) &= -J, \\ E(1, 0) &= -2J + j, \\ E(2, 1) &= -3J, \end{aligned} \quad (3)$$

with:

$$\begin{aligned}\hat{S}' &= \hat{S}_{\text{Cu1}} + \hat{S}_{\text{Cu2}}, \\ \hat{S} &= \hat{S}' + \hat{S}_{\text{Ni}},\end{aligned}\quad (4)$$

Since the ground state of the compound is the singlet (vide infra), it is not necessary to introduce local anisotropy or anisotropic interaction terms in (2). The Zeeman perturbation is:

$$H_Z = \beta \vec{H} \cdot (\mathbf{g}_{\text{Cu1}} \cdot \hat{S}_{\text{Cu1}} + \mathbf{g}_{\text{Ni}} \cdot \hat{S}_{\text{Ni}} + \mathbf{g}_{\text{Cu2}} \cdot \hat{S}_{\text{Cu2}}), \quad (5)$$

and the magnetic susceptibility is:

$$\begin{aligned}\chi_M T &= (2N\beta^2/k)[g_{1(1)}^2 \exp(J/kT) + g_{1(0)}^2 \exp((2J-j)/kT) + \\ &\quad 5g_2^2 \exp(3J/kT)]/[1 + 3\exp(J/kT) + 3\exp((2J-j)/kT) + \\ &\quad 5\exp(3J/kT)].\end{aligned}\quad (6)$$

The $\mathbf{g}_{S(S')}$ tensors are related to the local tensors through (Gatteschi and Bencini 1985):

$$\begin{aligned}\mathbf{g}_{1(1)} &= \mathbf{g}_2 = (\mathbf{g}_{\text{Cu1}} + \mathbf{g}_{\text{Cu2}} + 2\mathbf{g}_{\text{Ni}})/4, \\ \mathbf{g}_{1(0)} &= \mathbf{g}_{\text{Ni}}.\end{aligned}\quad (7)$$

The only role of j is to modify slightly $E(1, 0)$, the energies of the other three states remaining unchanged. Its influence on the magnetic properties is almost negligible, so that it cannot be determined by fitting the magnetic data of the Cu(II)Ni(II)Cu(II) species. On the other hand, j can be estimated from the magnetic properties of the Cu(II)Zn(II)Cu(II) species where Zn(II) replaces Ni(II). This compound behaves as a copper(II) binuclear complex with a singlet-triplet energy gap equal to j . j has been found to be in the range $0 > j > -1.6 \text{ cm}^{-1}$. The magnetic properties of $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ are shown in figure 5, where, to be homogeneous with the other curves of this paper,

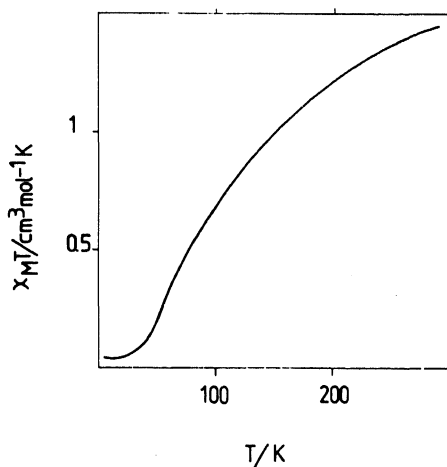


Figure 5. $\chi_M T$ versus T plot for $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$.

$$\underline{{}^5B_{2u}} - 3J = 296.1 \text{ cm}^{-1}$$

$$\underline{{}^3B_{1g}} - 2J = 197.4 \text{ cm}^{-1}$$

$$\underline{{}^3B_{2u}} - J = 98.7 \text{ cm}^{-1}$$

$$\underline{{}^1B_{2u}}$$

Figure 6. Spectrum of the low lying states in $[\text{Cu}_2\text{Ni}(\text{oxpn})_2(\text{H}_2\text{O})_2]\text{ClO}_4$.

we plotted $\chi_M T$ versus T . Upon cooling down, $\chi_M T$ continuously decreases and tends to a value very close to zero, confirming that the ground state is the singlet. The $\chi_M T$ versus T plot exhibits a maximum around 90 K, which is characteristic of a coupled molecular system with a diamagnetic ground state. The fitting of the data leads to $J = -98.7 \text{ cm}^{-1}$ with an average g -value of 2.12 and a spectrum of the low lying states as depicted in figure 6, where we indicated the orbital symmetry of the states, assuming a D_{2h} molecular symmetry.

The most interesting result concerning this complex is the large magnitude of the antiferromagnetic interaction between metal ions separated by about $5.1 \text{ \AA}$. In other words, the oxamido *bis* bidentate ligand has quite a remarkable ability to transmit the electronic effects between metal ions far away from each other. This problem has recently been reviewed (Kahn 1985a) and we do not intend to discuss it again here. We simply recall that the efficiency of *bis* bidentate ligands like

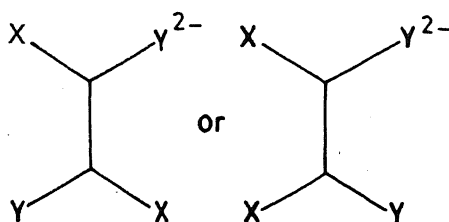


Chart 1.

with $X, Y = \text{O}, \text{S}$ or NR to propagate an antiferromagnetic interaction is due to the favorable relative orientations of the xy -type magnetic orbitals that point from the metal toward the four nearest neighbors and overlap of either side of the bridge, as shown in chart 2. It has also been shown that the less electronegative the X and Y groups are, the more delocalized the magnetic orbitals and the stronger the antiferromagnetic interaction (Kahn 1985a, Verdaguer *et al* 1985). So, the magnitude of the phenomenon varies as dithiooxalato $\text{C}_2\text{O}_2\text{S}_2^{2-} >$ oxamido $[\text{C}_2\text{O}_2(\text{NR})_2]^{2-} >$ oxamato $[\text{C}_2\text{O}_3(\text{NR})]^{2-} >$ oxalato $\text{C}_2\text{O}_4^{2-}$.

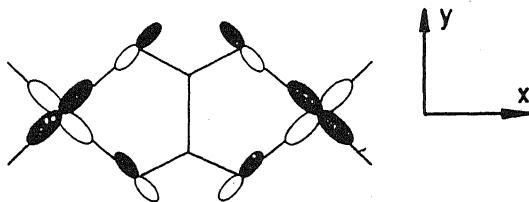


Chart 2.

2.3 $\{[Mn(Me_6[14]ane\ N_4)]_2Cu(pba)\}(CF_3SO_3)_2 \cdot 2H_2O$

A complex containing the Mn(II)Cu(II)Mn(II) triad with $S_{Mn} = 5/2$ and $S_{Cu} = 1/2$ has been synthesized (Pei *et al* 1986a). Its formula is $\{[Mn(Me_6[14]ane\ N_4)]_2Cu(pba)\}(CF_3SO_3)_2 \cdot 2H_2O$ and it is obtained by condensation of two moles of $[Mn(Me_6[14]ane\ N_4)](CF_3SO_3)_2$ with one mole of $Na_2[Cu(pba)] \cdot 6H_2O$. $Me_6[14]ane\ N_4$ is *d, l, 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecane* (Tait and Busch 1972) and *pba* is 1,3-propylene *bis* (oxamato) (Nonoyama *et al* 1976). The skeleton of the trinuclear unit is schematized in figure 7. Owing to the nature of the bridges, the Mn(II)Cu(II) interaction is expected to be strongly antiferromagnetic (see §2.2), which gives rise to a 9/2 ground state with the $(5/2, -1/2, 5/2)$ symbolic notation for the local spins. The magnetic behavior of this compound is shown in figure 8. As expected, $\chi_M T$ first decreases upon cooling with a very rounded minimum about 170 K, then increases in a rather abrupt fashion up to a high plateau with $\chi_M T = 12.1\text{ cm}^3\text{ mol}^{-1}\text{ K}$. This plateau exactly corresponds to what is expected for an $S = 9/2$ isolated state ($\chi_M T = 33 N\beta^2 g_{9/2(5)}^2 / 4k$) with $g_{9/2(5)} = 1.98$. $g_{9/2(5)}$ is related to the local tensors by:

$$g_{9/2(5)} = (6g_{Mn1} - g_{Cu} + 6g_{Mn2})/11 \quad (8)$$

Apparently, the zero field splitting within the ground state is very weak since $\chi_M T$ does not exhibit any deviation from the Curie law. This is confirmed by the EPR spectrum at 4.2 K where no fine interaction is detected. This spectrum exhibits the $\Delta M_s = \pm 1$ allowed transition at $g = 1.991$ and the $\Delta M_s = \pm 2, \pm 3$ and ± 4 forbidden transitions of decreasing intensity at half, third and quarter-field respectively. The theoretical expression for the magnetic susceptibility has been established from the spin state structure of figure 3 and the Zeeman perturbation expressed as:

$$H_Z = \beta \vec{H} \cdot (g_{Mn1} \cdot \hat{S}_{Mn1} + g_{Cu} \cdot \hat{S}_{Cu} + g_{Mn2} \cdot \hat{S}_{Mn2}) \quad (9)$$

The *g*-factors of the eleven spin states have been calculated as a function of the

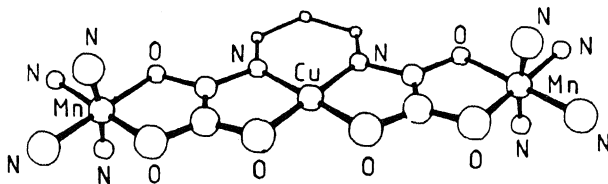


Figure 7. Trinuclear unit in $\{[Mn(Me_6[14]ane\ N_4)]_2Cu(pba)\}(CF_3SO_3)_2 \cdot 2H_2O$.

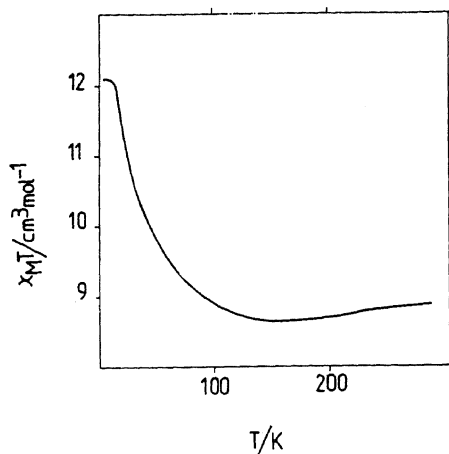


Figure 8. $\chi_M T$ versus T plot for $\{[\text{Mn}(\text{Me}_6[14]\text{ane } \text{N}_4)]_2\text{Cu}(\text{pba})\} (\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$.

$g_{\text{Mn}} = 2.03$ and $g_{\text{Cu}} = 2.10$. This Mn(II)Cu(II)Mn(II) complex is to our knowledge the molecular unit exhibiting the largest spin multiplicity in its ground state.

A Ni(II)Cu(II)Ni(II) complex similar to that of figure 7 has also been synthesized, Ni(II) replacing Mn(II). It has an $S = 3/2$ ground state and the $\chi_M T$ versus T plot exhibits the characteristic minimum of this type of antiferromagnetically coupled trinuclear species with irregular spin state structure. In this compound, the isotropic interaction parameter is found to be equal to $J = -135 \text{ cm}^{-1}$.

3. Ordered bimetallic chains

We have seen in §2.1 that a trinuclear species can have an irregular spin state structure with, in the case of antiferromagnetic interaction, a ground state which has not the lowest spin multiplicity. It follows that the temperature dependence of $\chi_M T$ displays a characteristic minimum. The most spectacular example is the antiferromagnetically coupled Mn(II)Cu(II)Mn(II) triad. This concept of irregular spin state structure can be extended to more complex systems like the ordered bimetallic chains. The first compound of this kind was reported in 1981 and opened new and very exciting perspectives in the field of magnetic systems (Gleizes and Verdaguer 1981). In the forthcoming sections, we shall present first the main theoretical ideas both at a qualitative, then the quantitative level: afterwards, we shall discuss the most significant experimental results reported so far.

3.1 Theory: qualitative approach

To introduce the main ideas (Verdaguer *et al* 1983), we consider an ordered and regular bimetallic ring $(AB)_N$ where N may become infinitely large. A and B symbolize magnetic metal ions surrounded by their nearest neighbor ligands, including the bridging ligands, with spins S_A and $S_B \neq S_A$ respectively. We also

assume that A and B have no first order angular momentum. The spin Hamiltonian in zero field appropriate to the problem is:

$$H = -J \sum_{i=1}^{2N} S_i \cdot S_{i+1}, \quad (10)$$

with :

$$S_{2i-1} = S_A,$$

$$S_{2i} = S_B,$$

$$\hat{S}_{2N+i} = \hat{S}_i.$$

In (10) local anisotropies and anisotropic interactions have been ignored.

We suppose first that J is negative. In this case, the state of lowest energy E_g may be schematized as:

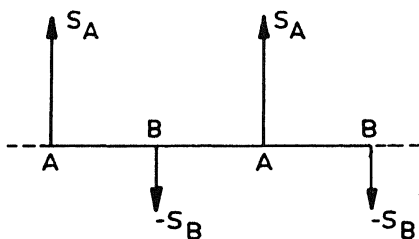


Chart 3.

with the spin $S_g = N(|S_A - S_B|)$. The state of highest energy E_e is as:

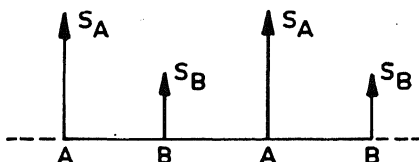


Chart 4.

with the spin $S_e = N(S_A + S_B)$. Between the two limits E_g and E_e , states with spins inferior to S_g do exist. In particular, there are states with $S = 0$ if the total number of unpaired electrons $2N(S_A + S_B)$ is even, one of them is schematized hereunder:

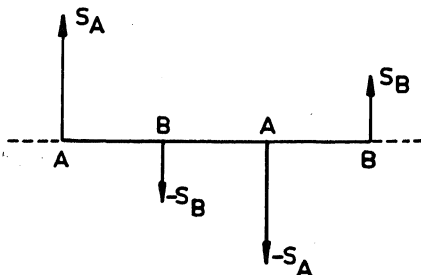


Chart 5.

or with $S = 1/2$, if this number is odd: In other words, for any $N \neq 1$, the spin state structure is always irregular. This irregularity increases with N and $|S_A - S_B|$ since

S_g is proportional to those two quantities whereas the lowest spin is always 0 or $1/2$. Let us examine now the consequences of this irregularity as far as the temperature dependence of $\chi_M T$ is concerned, χ_M being the magnetic susceptibility per AB unit. The Zeeman perturbation to add to (10) is:

$$H_Z = \beta \hat{H} \cdot \sum_{i=1}^N (\mathbf{g}_{A2i-1} \cdot \hat{S}_{2i-1} + \mathbf{g}_{B2i} \cdot \hat{S}_{2i}). \quad (11)$$

Since, in this section, we restrict ourselves to a qualitative approach, we assume that the $\mathbf{g}_A$ and $\mathbf{g}_B$ tensors are isotropic with the same principal value g . At very high temperature, when $kT \gg |J|$, $\chi_M T$ tends to the $(\chi_M T)_{HT}$ limit corresponding to the superposition of the uncoupled A and B fragments. This limit is:

$$(\chi_M T)_{HT} = (N\beta^2 g^2 / 3k) \cdot [S_A(S_A + 1) + S_B(S_B + 1)]. \quad (12)$$

The low temperature limit, when $kT/|J|$ approaches zero, is:

$$(\chi_M T)_{LT} = (N\beta^2 g^2 / 3k) [N(S_A - S_B)^2 + |S_A - S_B|]. \quad (13)$$

For $N = N_0$ defined as:

$$N_0 = (S_A^2 + S_B^2 + 2S_-) / (S_A - S_B)^2, \quad (14)$$

where S_- is the smaller of S_A and S_B , the limits $(\chi_M T)_{HT}$ and $(\chi_M T)_{LT}$ are equal. For $N > N_0$, $(\chi_M T)_{LT}$ is superior to $(\chi_M T)_{HT}$ and when N tends to the infinite, $(\chi_M T)_{LT}$ diverges. Upon cooling down from the high temperature, one depopulates first the state of highest spin multiplicity so that $\chi_M T$ decreases. Therefore, one is led to the following fundamental result: *For a chain of alternated and antiferromagnetically coupled spins S_A and S_B , upon cooling down, $\chi_M T$ first decreases, then reaches a minimum for a finite temperature and finally diverges when T approaches zero.* This behavior is valid for any couple S_A and $S_B \neq S_A$, provided that there is no compensation of the local magnetic moments (see §3.2). Another way to express the same result is to say that at high temperature, $\chi_M T$ tends toward the paramagnetic limit; the minimum of $\chi_M T$ corresponds to a short-range order state where the spins S_A and S_B of adjacent ions are antiparallel, but without correlation between neighboring AB units. When T decreases, the correlation length within the chain increases, leading to a magnetic short-range order symbolized by $(S_A, -S_B)_N$. Such a situation may be defined as the *one-dimensional ferrimagnetism*. Below the temperature of the minimum of $\chi_M T$, the magnetic behavior is qualitatively equivalent to what happens in a chain of N spins $|S_A - S_B|$ ferromagnetically coupled. This point, which is of utmost importance, will be developed further.

If the intrachain interaction is ferromagnetic ($J > 0$), the order of the spin levels is reversed and no extremum of the $\chi_M T$ versus T plot can be predicted a priori. In fact, no compound of that sort has been reported so far and in the following, we shall ignore this situation.

3.2 Theory: quantitative approach

Several quantitative approaches of the magnetic susceptibility of ordered bimetallic chains have been proposed so far. The first one consists of carrying out the

calculation on $(AB)_N$ rings of increasing size with quantum spins S_A and S_B and to extrapolate to $N \rightarrow \infty$ (Verdaguer *et al* 1983; Drillon *et al* 1983b). This requires that for each N the Hamiltonian (10) is diagonalized by using the microstates as basis sets with M_s varying from 0 or 1/2, according as $2N(S_A + S_B)$ is even or odd, up to $N(S_A + S_B)$, as done for the first time by Orbach (1959) for a chain of spins 1/2. This leads to the energies $E_i(S)$ of the spin states and to their multiplicity. In the hypothesis where the average g -factors, g_A and g_B , are equal, the calculation of the magnetic susceptibility is then straightforward since all the spin states have the same g -factor and the spin labels S are good quantum numbers even in the presence of the Zeeman perturbation. The method is an extension of the work of Bonner and Fisher (1964) concerning regular chains of spins 1/2. For $g_A \neq g_B$, not only each spin state has a given g_s -factor but also the Zeeman perturbation couples the components of the same M_s belonging to different spin states, which introduces nonzero second-order Zeeman coefficients in the calculation of the susceptibility. This method, even by taking into account the full D_N symmetry of the problem, is severely limited by the storage capacity of the computers, as well as by the computing time. The problem which has been studied best is the one with $S_A = 1/2$, $S_B = 1$. Drillon *et al* (1983b) performed the calculation up to $N = 5$ and extrapolated for $N \rightarrow \infty$. The result for $g_A = g_B$ is shown in figure 9. The minimum of $\chi_M T$ is obtained for $kT/|J| = 0.570$. In the very low temperature range, $\chi_M T$ diverges according to a power law $T^{-0.80}$, which coincides with the law found for a chain of ferromagnetically coupled spins 1/2. Drillon *et al* (1983b) also investigated the effect of $g_A/g_B \neq 1$ and found that for $g_A/g_B = 2.66$, there is an exact compensation of the magnetic moments associated with A and B respectively. The ground state becomes nonmagnetic and $\chi_M T$ continuously decreases down to zero upon cooling. The $(AB)_N$ ring chain technique has also been utilized for the $S_A = 1/2$, $S_B = 5/2$ (Drillon *et al* 1984) and $S_A = 1$, $S_B = 5/2$ (Drillon *et al* 1986) situations but in both cases only up to $N = 3$. Very quickly, the problem becomes untractable and alternative methods are indispensable.

The simplest method consists of considering that both $\hat{S}_A$ and $\hat{S}_B$ are classical spins with g_A^e and g_B^e effective g -factors and a J^e effective interaction parameter. The

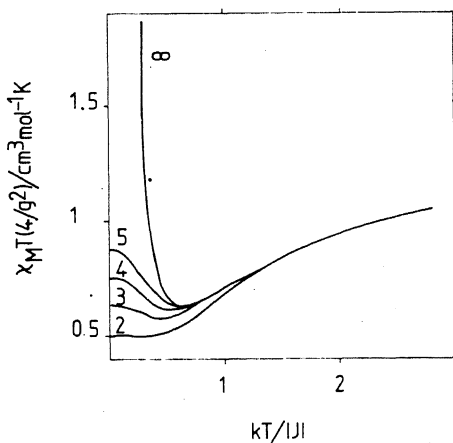


Figure 9. $\chi_M T(4/g^2)$ versus $kT/|J|$ plot for antiferromagnetically coupled $(AB)_N$ ring chains of spins $S_A = 1/2$, $S_B = 1$.

effective parameters are related to the actual parameters through:

$$g_A^e = g_A[S_A(S_A + 1)]^{1/2}, \quad (15)$$

and a similar relation for g_B^e , and:

$$J^e = J[S_A(S_A + 1)S_B(S_B + 1)]^{1/2}. \quad (16)$$

An analytical expression for the magnetic susceptibility has been derived by Drillon *et al* (1983a). This expression is:

$$\chi_M T = \frac{N\beta^2}{3k} \left(g^2 \frac{1+u}{1-u} + \delta^2 \frac{1-u}{1+u} \right), \quad (17)$$

with:

$$\begin{aligned} g &= \frac{1}{2}(g_A^e + g_B^e), \\ \delta &= \frac{1}{2}(g_A^e - g_B^e), \\ u &= \coth(J^e/kT) - (kT/J^e) \end{aligned} \quad (18)$$

For $\delta = 0$, (17) reduces to the known expression for a regular chain of classical spins (Fischer 1974). For $\delta \neq 0$ and $J < 0$, a minimum in the $\chi_M T$ versus T plot appears and when T approaches zero, $\chi_M T$ diverges in a ferromagnetic-like fashion. The divergence law is $\delta^2 T^{-1}$. The validity of (17) is the same as the validity of the classical spin approximation. The larger S_A and S_B are, the better the relation (17). For $S_B = 5/2$, (17) is likely to be valid if $S_A = 2$, may be also if $S_A = 3/2$ or 1 but is certainly a very poor approximation if $S_A = 1/2$.

The $S_A = 1/2$, $S_B = 5/2$ case has been treated in quite an elegant way by Seiden (1983) and Verdaguer *et al* (1984). The method consists of taking S_A as a quantum spin and S_B as a classical spin. We cannot present here the details of the calculation that is very elaborated. This calculation does not lead to an analytical expression but can be solved numerically. The following empirical relation has been proposed to fit the numerical results (Gleizes and Verdaguer 1984).

$$\begin{aligned} \chi_M T &= (g^2/4)(4.75 - 1.62370X + 2.05042X^2 - 4.52588X^3 \\ &\quad - 8.64256X^4)/(1 + 0.77968X - 1.56527X^2 - 1.57333X^3 \\ &\quad - 0.11666X^4) \end{aligned} \quad (19)$$

with:

$$X = |J|/kT. \quad (20)$$

Equation (19) is only valid for $J < 0$. The plot of $\chi_M T$ ($4/g^2$) versus $kT/|J|$ is represented in figure 10. $\chi_M T$ exhibits a rounded maximum for $kT/|J| = 2.98$. Upon cooling below the temperature of the minimum, $\chi_M T$ diverges in an abrupt way, following a law in $T^{-0.69}$. In this quantum-classical approach, the g_A and g_B factors were assumed to be equal.

In all the approaches mentioned above, the local anisotropies of the ions with S_A (or S_B) $> 1/2$ were neglected. Such an approximation can lead to a poor description of the low temperature range if $|D/J|$ is not very small. In the specific case $S_A = 1/2$, $S_B = 1$, it has been shown that the larger $|D/J|$ is, the more the

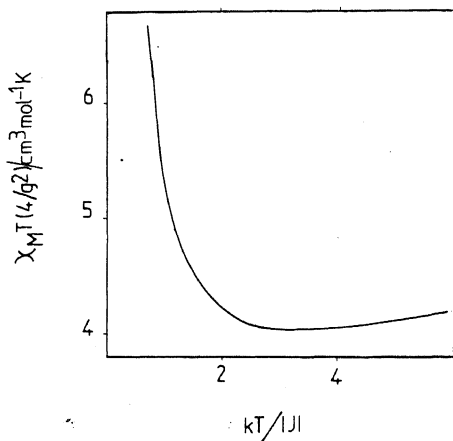


Figure 10. $\chi_M T (4/g^2)$ versus $kT/|J|$ plot for an infinite $(AB)_N$ chain with $S_A = 1/2$, $S_B = 5/2$.

minimum of $\chi_M T$ is shifted toward the low temperatures (Verdaguer *et al* 1983). An eventual anisotropic interaction would have the same effect. Finally, all the calculations deal with perfectly isolated $(AB)_N$ chains. In fact, much above the critical temperature where a three-dimensional order appears, the interchain interaction may substantially modify the magnetic behavior. If the interchain interaction couples the chains in an antiparallel fashion, as it is most often the case, the divergence of $\chi_M T$ is stopped with a maximum of $\chi_M T$ occurring just above the critical temperature. If this interchain interaction is large, the minimum of $\chi_M T$ can be hidden.

3.3 $\text{CuMn}(\text{dto})_2(\text{H}_2\text{O})_3 \cdot 4.5\text{H}_2\text{O}$

The first structurally characterized ordered bimetallic chain is $\text{CuMn}(\text{dto})_2(\text{H}_2\text{O})_3 \cdot 4.5\text{H}_2\text{O}$ with dto = dithiooxalato. This compound has been investigated by Gleizes and Verdaguer (1984) and Verdaguer *et al* (1984). The structures of two adjacent chains as well as the detail of the structure of one of the chains are shown in figure 11. Cu(II) is tetracoordinated with a planar environment and Mn(II) is heptacoordinated in a rather unusual fashion. The metal centers are bridged by the dithiooxalato ligand, the oxygen atoms being bound to manganese and the sulfur atoms to copper. The magnetic data shown in figure 12 closely follow the theoretical predictions. Upon cooling down, $\chi_M T$ decreases, reaches a weekly pronounced minimum around 130 K and increases down to 7.5 K. $\chi_M T$ is then equal to $11.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Finally, below 7.5 K, $\chi_M T$ decreases rapidly. In the range 7.5–300 K, these magnetic data are well fitted by the quantum-classical approach presented in the preceding section, with $J = -30.3 \text{ cm}^{-1}$ and $g = 1.90$. The maximum of $\chi_M T$ at 7.5 K is clearly due to an antiferromagnetic interaction between ferrimagnetic like chains. Magnetization studies at 1.3 and 4.2 K show a saturation corresponding to the spin $|S_A - S_B| = 2$ per CuMn unit. The relatively large $|J|$ value found in $\text{CuMn}(\text{dto})_2(\text{H}_2\text{O})_3 \cdot 4.5\text{H}_2\text{O}$ is due to the remarkable efficiency of the dithiooxalato bridge to propagate an antiferromagnetic interaction between metal centers with xy -type magnetic orbitals.

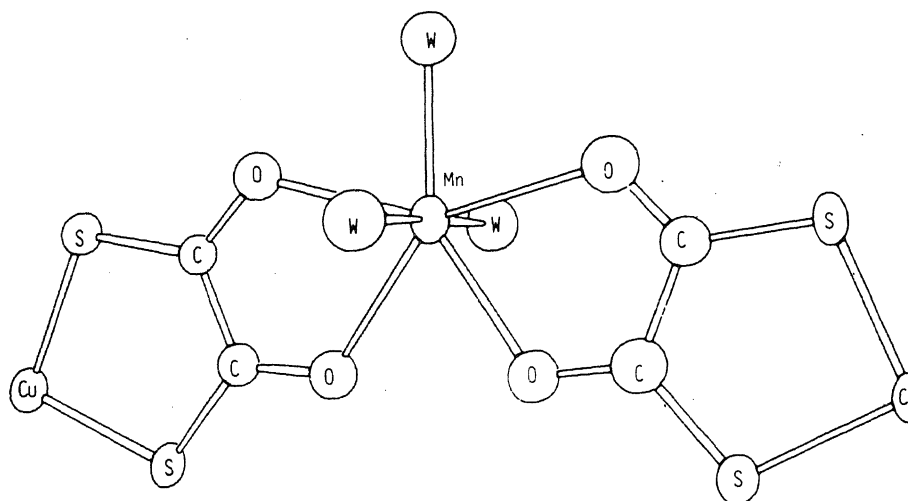
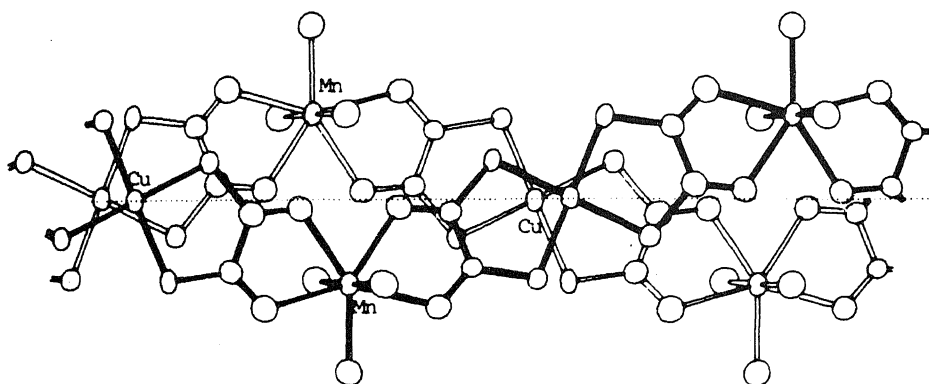


Figure 11. Crystal structure of $\text{CuMn(dto)}_2(\text{H}_2\text{O})_3 \cdot 4.5\text{H}_2\text{O}$.

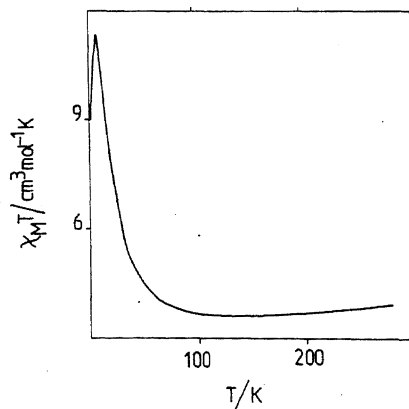


Figure 12. $\chi_M T$ versus T plot for $\text{CuMn(dto)}_2(\text{H}_2\text{O})_3 \cdot 4.5\text{H}_2\text{O}$.

3.4 $\text{CuMn(pba)}(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ and related compounds

Another example of Cu(II)Mn(II) ordered bimetallic chain is provided by $\text{CuMn(pba)}(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$, with pba = 1,3-propylene bis(oxamato). The structure of the chain is given in figure 13 and that of the crystal lattice in figure 14 (Pei *et al* 1986b). Cu(II) is here in a square pyramidal environment and Mn(II) in a more classical octahedral environment. The metal centers are aligned along the b axis of

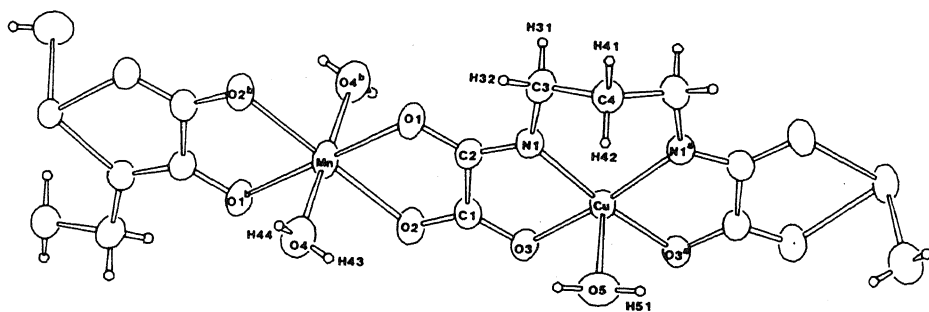


Figure 13. Crystal structure of $\text{CuMn(pba)}(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$.

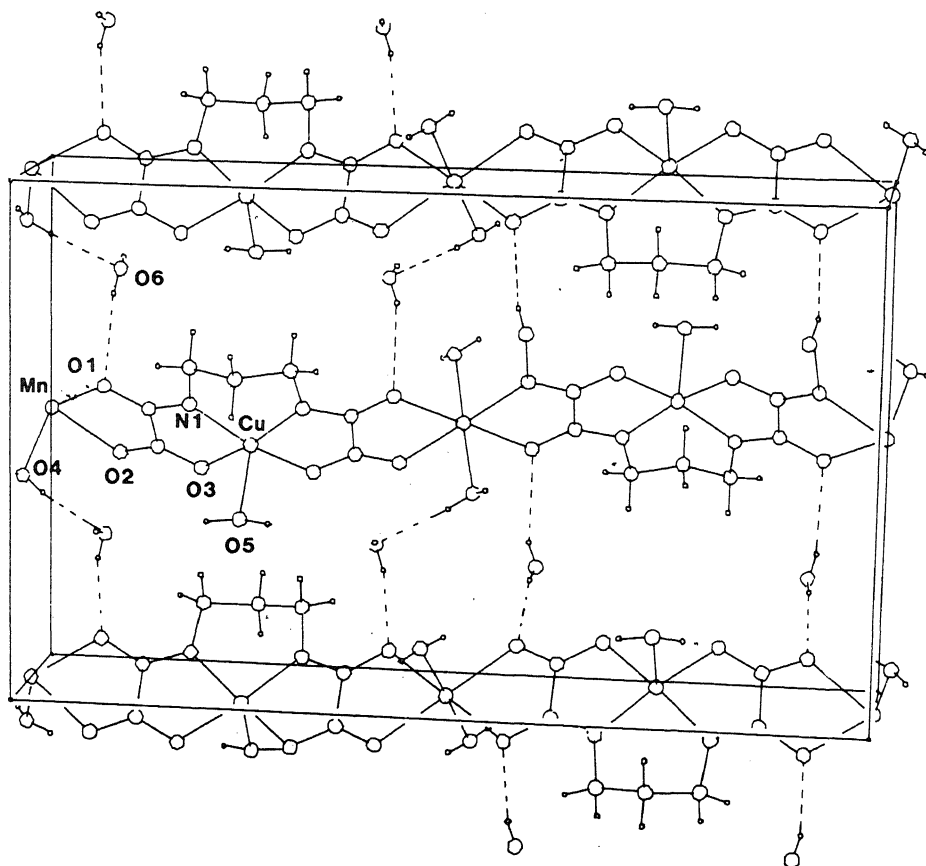


Figure 14. Crystal packing for $\text{CuMn(pba)}(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$.

the orthorhombic structure, whereas in the previous example they form zigzag chains. Within the chains, two nearest neighbor metal ions are bridged by an oxamato group with a Cu . . . Mn separation of 5.41 Å. The chains are linked together by hydrogen bonding involving the oxygen atoms of the bridge and the coordinated as well as the non-coordinated water molecules. The relative positions of two adjacent chains are such that, if one takes an ion of a given type, Cu(II) or Mn(II), belonging to a chain, the nearest neighbor ion belonging to the other chain is an ion of the same type.

As expected, the $\chi_M T$ versus T plot exhibits a rounded minimum about 115 K and below this temperature a very fast increase upon cooling. Again a maximum of $\chi_M T$ is observed, but at a much lower temperature than in the previous case, namely 2.3 K instead of 7.5 K. This indicates that the interchain interaction is weaker in this compound than in the previous one. The fitting of the magnetic data above 4.2 K leads to $J = -23.4 \text{ cm}^{-1}$ with $g = 1.96$ (Pei *et al.*, 1987). This J value, although still important, is significantly smaller in its absolute value than that found in $\text{CuMn(dto)}_2 (\text{H}_2\text{O})_{3.45} \text{H}_2\text{O}$. This is due to the fact that the magnetic orbital around copper(II) is delocalized more towards the sulfur atoms of the dithiooxalato bridge in the dto derivative than towards the nitrogen and oxygen atoms of the oxamato bridge in the pba derivative, owing to the weak electronegativity of sulfur with regard to nitrogen and oxygen.

Let us examine now the mechanism of the interchain coupling. Owing to the relative positions of two adjacent chains, the dominant interchain interactions are Cu(II)Cu(II) and Mn(II)Mn(II). If these interactions are antiferromagnetic, then the spin structure will be as:

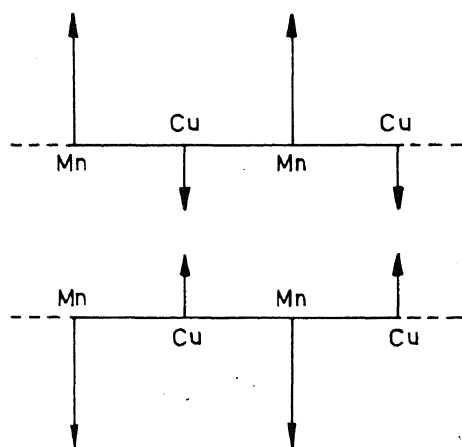


Chart 6.

with a cancellation of the spins at the scale of the lattice. This leads to the fall of $\chi_M T$ below 2.3 K. Now, if by using some chemical stratagem, we can displace every other chain in the crystal lattice by half of a repeat unit along the b axis, then the interchain interactions will occur between metal ions of different nature and, provided that these interactions are again antiferromagnetic, the spin structure will be as:

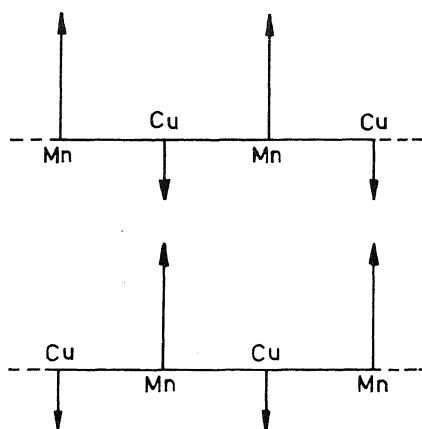
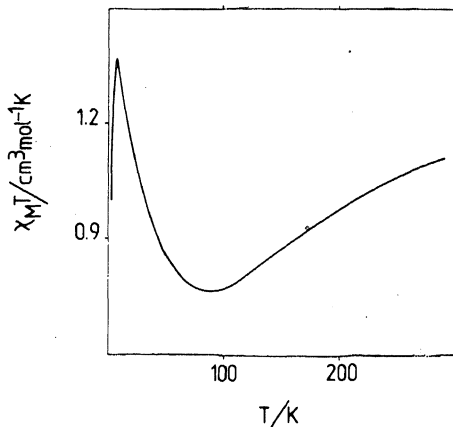


Chart 7.

with, at the scale of the lattice, all the $5/2$ spins aligned along the same direction. Such a system should exhibit a three-dimensional ferromagnetic (or ferrimagnetic) order below a critical temperature. Such a situation could be at the origin of the quite remarkable magnetic properties of $\text{CuMn}(\text{bpaOH}) \cdot 3\text{H}_2\text{O}$ (Pei *et al.*, 1986c). Chemically, the only difference between this compound and $\text{CuMn}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ is the replacement of the methylene group of the propylene chain by CHOH . Above 60 K, the pba and pbaOH derivatives exhibit the same magnetic properties with the characteristic minimum of $\chi_M T$ around 115 K. On the other hand, below 60 K, $\chi_M T$ for $\text{CuMn}(\text{bpaOH}) \cdot 3\text{H}_2\text{O}$ increases in a much more abrupt fashion and reaches an extraordinarily high value at 4.2 K. $\chi_M T$ is then larger than $100 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Magnetization studies in very low field ($H = 0.03 \text{ G}$) show that the compound orders ferromagnetically at 4.6 K. As is usual, the ferromagnetic order is destroyed by the magnetic field, even when H is as small as 1 G. $\text{CuMn}(\text{bpaOH}) \cdot 3\text{H}_2\text{O}$ may be considered as one of the first genuine molecular ferromagnets. The crystal structure of $\text{CuMn}(\text{pba OH}) \cdot 3\text{H}_2\text{O}$ has now been solved. It actually shows a displacement of every other chain by roughly half

Figure 15. $\chi_M T$ versus T plot for $\text{CuNi}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$.

of a repeat unit along one of the directions perpendicular to the chain axis (Pei *et al.*, 1986c).

The $\text{CuNi(pba)(H}_2\text{O)}_3 \cdot 2\text{H}_2\text{O}$ chain with Ni(II) replacing Mn(II) in the structure of figure 13 has also been prepared and studied (Pei *et al.*, 1987). The $\chi_M T$ versus T plot is shown in figure 15. It exhibits the characteristic minimum at 83 K and below this temperature $\chi_M T$ increases rapidly up to a maximum at 7.3 K, reflecting again an interchain interaction. The fitting of the magnetic data in the 10–300 K temperature range using the ring chain approach leads to $J = -82.7 \text{ cm}^{-1}$ with $g = 2.17$.

4. Toward the design of molecular ferromagnets

One of the main challenges in the field of molecular materials is the design of molecular ferromagnets. For that, a strategy immediately comes to mind, namely the achievement of ferromagnetic interactions between the nearest neighbor ions at the scale of the whole lattice. If so, the system will order ferromagnetically below a critical temperature. Such ferromagnetic interactions between nearest neighbors may arise either from the strict or from the accidental orthogonality of the magnetic orbitals (Kahn 1985a; Journaux *et al.* 1983). Both types of orthogonality are difficult to realize. It is indeed well established that in most of the cases, the interaction between two nearest neighbor ions is antiferromagnetic. In a certain sense, the achievement of a ferromagnetic interaction requires going against a natural trend which favors pairing of the electrons in molecular orbitals of low energy. Therefore, it was important to find an alternative strategy to design molecular systems with high spin multiplicity in the ground state and to develop this strategy up to the design of molecular ferromagnets. Such a strategy emerges from the concept of irregular spin state structure. It consists of imposing the parallel alignment of local spin 5/2 [Mn(II) or Fe(III)] owing to an antiferromagnetic interaction with local spin 1/2[Cu(II)]. In some way, the small spins 1/2 polarize the big spins 5/2 along the same direction. This leads to a 9/2 ground state for a Mn(II)Cu(II)Mn(II) trinuclear unit, to a one-dimensional ferrimagnetic short range order for the Cu(II)Mn(II) chain and to the onset of a ferromagnetic order when a small Cu(II)Mn(II) interchain interaction superimposes on the dominant Cu(II)Mn(II) intrachain interactions. It is quite remarkable that the $S_A = 1/2$, $S_B = 5/2$ couple is the most appropriate for obtaining a ferromagnetic like behavior in the frame of this strategy whereas the interaction between those two ions is most likely antiferromagnetic (Journaux *et al.* 1983). In fact, the more pronounced the Cu(II)Mn(II) antiferromagnetic interaction is, the more efficient the polarization of the S/2 spins along the same direction. In this respect, the *bis* bidentate ligands like dithiooxalato or oxamato are particularly suitable for this purpose. Not only do they give strong antiferromagnetic interactions (see §2.2) but their chemistry is also very flexible.

$\text{CuMn(bpaOH)} \cdot 3\text{H}_2\text{O}$ is apparently the first molecular ferromagnet obtained according to this strategy, with a Curie temperature of 4–6 K. This result is quite preliminary in the sense that the other physical properties of the compound are not yet known. The thorough investigation of this compound as well as the design of other systems of this kind with, if possible, a higher magnetic order temperature,

are two directions along which several groups are engaged. The difficulty along this way arises from the fact that there is no magnetic order at one or two dimensions, but only at three dimensions. Therefore the chemist has to work in terms of crystal engineering, and not only of molecular engineering.

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Low temperature high field magnetisation studies on metalloporphyrins

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Abstract. Magnetisation studies at very high magnetic fields and low temperatures on several high-spin iron(III) and manganese(III) porphyrins are reviewed. The usefulness of these studies in understanding the properties of the ground electronic state of the metal ion is discussed.

Keywords. Magnetisation; iron porphyrins; zero-field splitting; magnetic saturation; exchange interaction.

1. Introduction

Metalloporphyrins are a class of biologically important molecules which form the prosthetic group in heme proteins. The metal ion in the prosthetic group is the site of the biological activity in many of them, and its electronic structure determines many of their biological functions. This factor has led to considerable interest in the physico-chemical properties and electronic structure of these metalloporphyrins (Smith 1975; Dolphin 1978).

Study of magnetisation at low temperatures and high magnetic fields is a powerful method to probe the electronic structure, especially the ground state, of the metal ion in the paramagnetic hemes (Mitra 1983). At very high magnetic fields the Zeeman splitting of the ground level becomes sufficiently large to cause mixing between the close-lying spin-multiplets and provide information about the ground state. The experiments must however be done at temperatures below 10 K when only the ground state is preferentially populated. In this article we discuss results of high-field magnetisation studies carried out at very low temperatures on some iron and manganese porphyrins.

Magnetisation (σ) of a paramagnetic ion is given by $\sigma = \chi \cdot H$, where χ is the magnetic susceptibility. At very high-fields and at low-temperatures (i.e. in the saturation region), the magnetic susceptibility is field-strength dependent. Magnetisation is therefore a more appropriate quantity to define the magnetic properties in this region.

The following abbreviations of the porphyrin ligands have been used in this paper: TPP, tetraphenylporphyrin; OEP, Octaethylporphyrin; PP, protoporphyrin IX; DPDME, deuteroporphyrindimethylester.

2. Experimental

Measurement of magnetisation is essentially the same as the measurement of magnetic susceptibility and can be performed using a Faraday or vibrating sample

magnetometer or even a SQUID susceptometer. Magnetic fields as high as 80 kOe can easily be obtained using superconducting magnets which also provide a cryostatic arrangement for measurements at different temperatures. During magnetisation measurements on polycrystalline samples some precautions must be taken. At very low temperatures the polycrystallites of anisotropic samples tend to preferentially orient in high magnetic fields, making the measurement of average magnetisation difficult. To overcome this problem measurements are made on a homogeneous mull of metalloporphyrins in diamagnetic vaseline frozen at low temperature outside the magnetic field. This ensures that the polycrystallites are randomly oriented in the vaseline mull and would remain so fixed even at very high magnetic fields. Alternatively, the measurements can be done on highly compressed tablets of the samples.

The magnetisation is usually expressed as reduced moment $\langle \mu \rangle = \sigma/N\beta$ in conformity with the Brillouin function (see later). The effective average magnetic moment $\bar{\mu}_{\text{eff}}$ reported in this article generally refers to measurements carried out at low magnetic field ($H < 10$ kOe).

3. Theoretical aspects

The magnetic moment of a paramagnetic ion can be given by

$$M = Ng\beta S \left[\frac{2S+1}{2S} \coth \left(\frac{2S+1}{2S} y \right) - \frac{1}{2S} \coth \frac{y}{2S} \right]$$

$$= Ng\beta S B_S(y),$$

where $y = g\beta SH/kT$. Here the expression $B(y)$ is usually called the Brillouin function. For very large values of $H/T \rightarrow \infty$, $(M/N\beta) \rightarrow gS$. Thus for $g = 2$ the saturation moment for $S = 5/2$ would be 5.0 BM, and for $S = 2$, 4.0 BM. A theoretical plot of the moment is shown in figure 1. This plot is strictly for free-ions, i.e., where the effects of crystal fields have been neglected. For $S = 1/2$, the ground state is a spin-doublet (with no orbital degeneracy), and the effect of crystal fields is negligible. Experimental results for such spin systems are found to obey the Brillouin curve very closely. However for $S \geq 1$, a sizeable zero-field splitting of the ground state is expected because of the combined effect of crystal field and spin-orbit coupling. This zero-field splitting is known to be very large in metalloporphyrins (Mitra 1983), which would cause large deviations in the expected behaviours from those in figure 1.

The magnetisation for a $S \geq 1$ spin system can be calculated by following spin-Hamiltonian formalism, which includes the effect of zero-field splitting in axial symmetry,

$$H = DS_z^2 + g\beta H.S, \quad (1)$$

where D is the zero-field splitting parameter. While calculating magnetisation using (1), two points must be considered. One is that at very high fields and low temperatures, magnetisation (or magnetic susceptibility) cannot be calculated using the Van Vleck equation which assumes $\beta H \ll kT$. Instead the thermodynamic equation

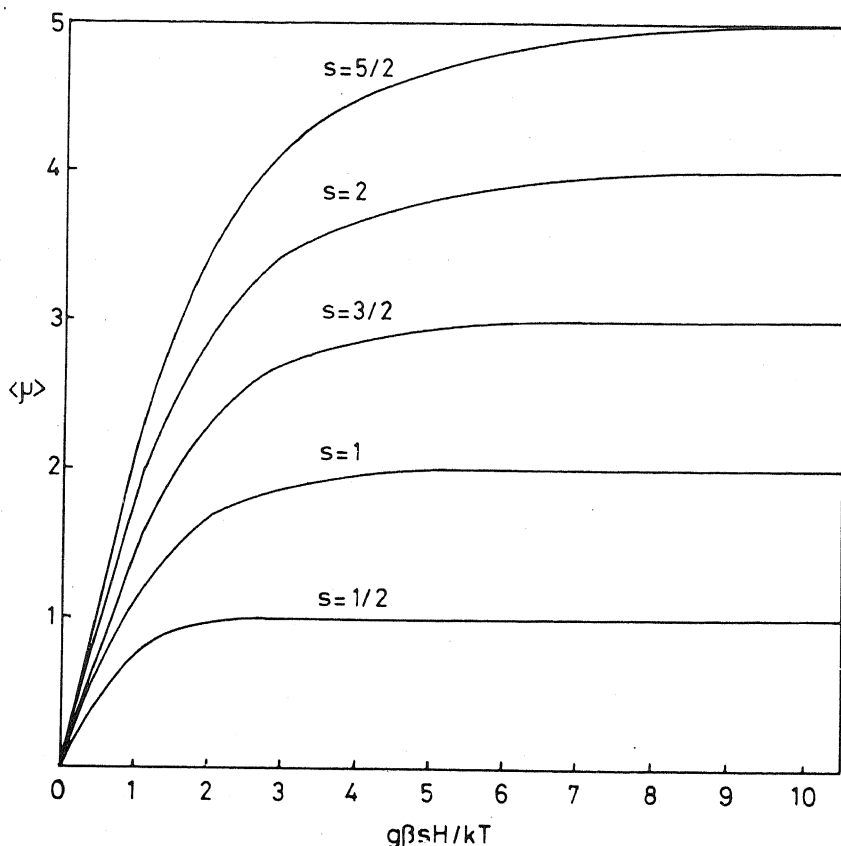


Figure 1. Brillouin function plot for magnetisation of $S = 5/2$ to $S = 1/2$.

$$\sigma = \chi \cdot H = -N \sum_i \left(\frac{\partial E_i}{\partial H} e^{-E_i/kT} \right) / \sum_i \left(e^{-E_i/kT} \right)$$

should be used (Marathe and Mitra 1973). Further in calculating the average magnetisation the usual procedure of averaging, i.e. $\bar{\sigma} = (\sigma_{\parallel} + 2\sigma_{\perp})/3$, may lead to significant errors at lower temperatures and higher fields (Marathe and Mitra 1974; Varmass and Groeneveld 1974), so, a spatial averaging technique should be used for calculating average σ (Marathe and Mitra 1974).

4. Results and discussion

4.1 High-spin iron(III) porphyrins

Magnetisation of several high-spin porphyrins has been reported over an extended range of temperature and magnetic field. The results are briefly discussed here.

Tetraphenylporphinato iron(III) halides: The average magnetisation of tetraphenylporphinato iron(III) chloride, Fe(TPP)Cl, and tetraphenylporphinato iron(III) bromide, Fe(TPP)Br, has been reported over 2–20 K and 10–50 kOe

(Behere and Mitra 1980a; Behere *et al* 1979; Birdy *et al* 1983). Both these molecules have similar stereochemical geometry with the iron atom being five-coordinated and lying appreciably above the mean plane of the porphyrin core (figure 2). The temperature dependence of their effective magnetic moment is very similar, showing sharp decrease in $\bar{\mu}_{\text{eff}}$ below 60 K (figure 3). At 4.2 K the $\bar{\mu}_{\text{eff}}$ has the values of 4.8 and 4.6 BM, respectively, for the chloro and bromo complexes. The decrease in $\bar{\mu}_{\text{eff}}$ at lower temperatures is characteristic of large zero-field splitting of the 6A_1 ground state of the ferric ion (figure 4). The magnetisation data at various fields are summarised in figures 5 and 6.

At 10 kOe the magnetisation varies linearly with temperature. As the field increases, deviation from linearity increases so much that for $H \geq 40$ kOe the magnetisation reaches complete saturation below 4 K. For Fe(TPP)Br where complete saturation is achieved, the saturation moment is $\langle \mu \rangle_{\text{sat}} = 3.0$ BM. For Fe(TPP)Cl the measurements extend down to only 4.2 K and complete saturation has not been achieved though the trend is clear (figure 5). The saturation moments together with other relevant data are listed in table 1. The low value of saturation moment is clearly a consequence of large zero-field splitting (ZFS).

The magnetisation has been calculated on spin Hamiltonian and crystal field models. For Fe(TPP)Br, a large value of ZFS, $D = 12.5 \text{ cm}^{-1}$ has been deduced

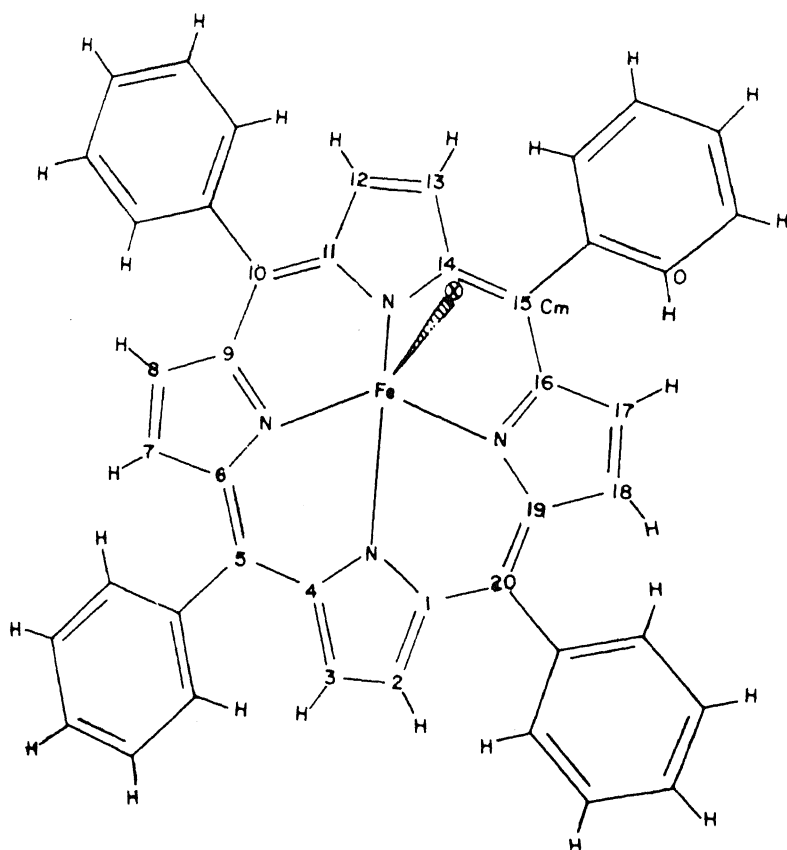


Figure 2. Molecular structure of Fe(TPP)X.

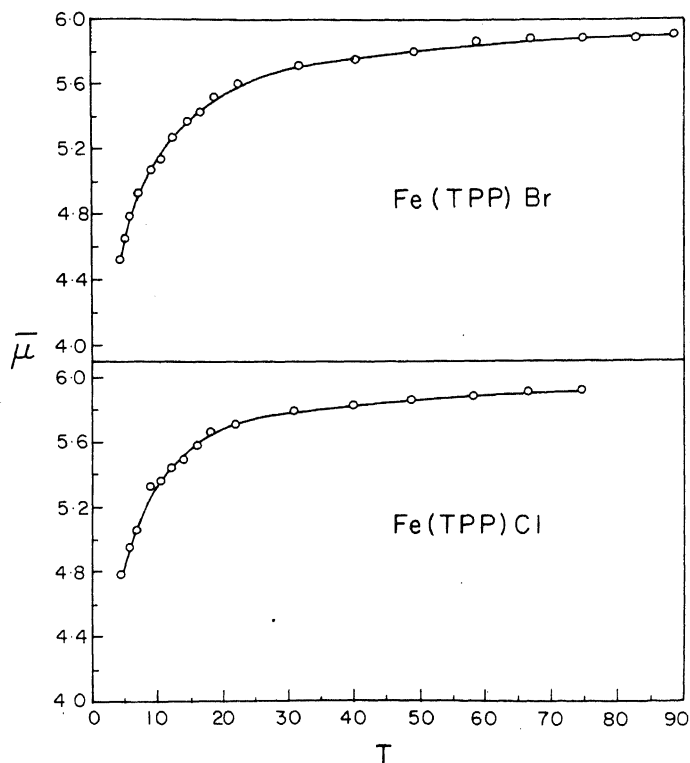


Figure 3. Temperature dependence $\bar{\mu}_{\text{eff}}$ for Fe(TPP)Cl and Fe(TPP)Br.

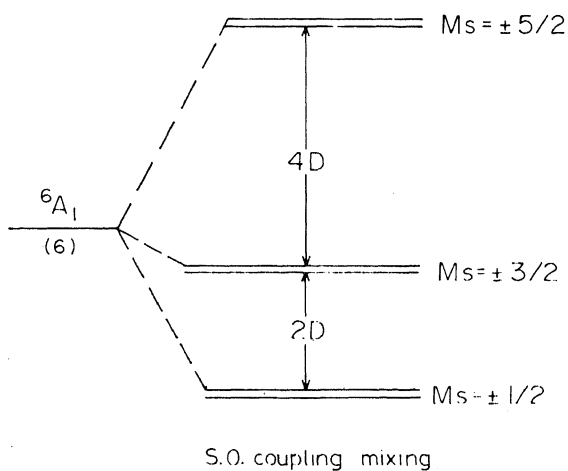


Figure 4. Zero-field splitting in iron(III) porphyrins (d^5 electron configuration with 6A_1 ground state).

(Behere *et al* 1979). The value is close to that deduced from high temperature single crystal susceptibility data (Behere *et al* 1979; Birdy *et al* 1983). For Fe(TPP)Cl a

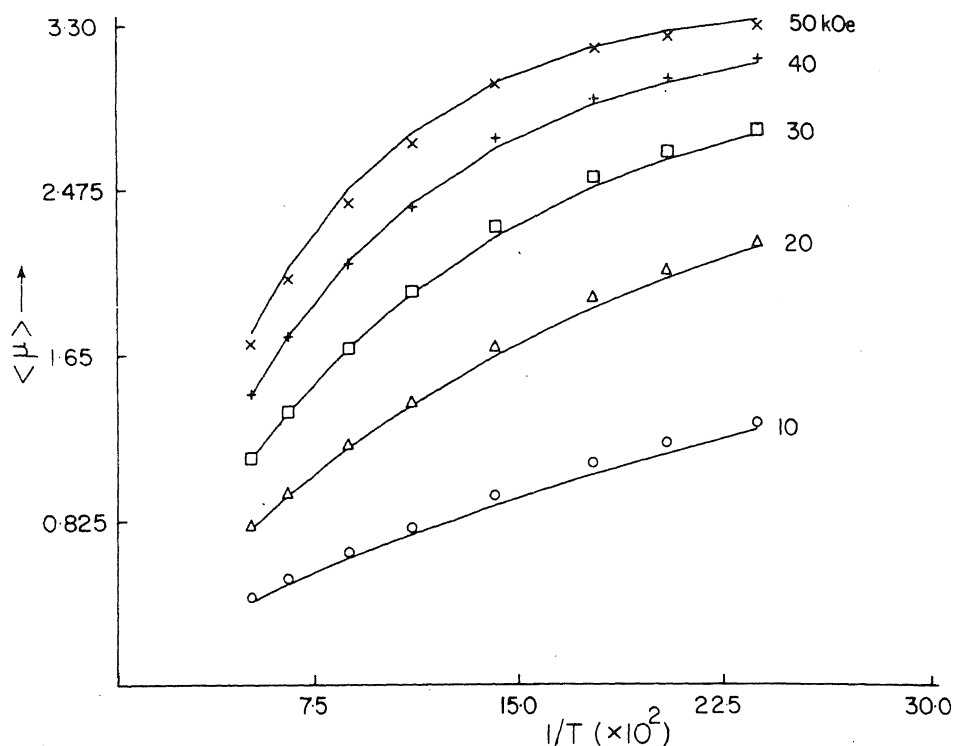


Figure 5. Magnetisation of Fe(TPP)Cl down to 4.2 K (Behere and Mitra 1980a). Solid curves are calculated for $D = 8.0 \text{ cm}^{-1}$.

value $D = 8.0 \text{ cm}^{-1}$ was deduced from the magnetisation study (Behere and Mitra 1980a; Birdy *et al* 1983), while the single crystal susceptibility measurements yielded $D = 6.0 \text{ cm}^{-1}$ (Behere *et al* 1977; Behere and Mitra 1979). The discrepancy is significant and has been attributed to the possible effects of magnetic exchange interaction (Behere and Mitra 1980a).

The molecular stacking in Fe(TPP)Cl is interesting in that half of the molecules in the lattice are stacked in a Fe-Cl.... Cl-Fe pseudo-dimeric fashion (figure 7). This long path appears to provide a route for occurrence of the magnetic exchange interaction through a superexchange mechanism. A further evidence of magnetic exchange in Fe(TPP)Cl comes from measurement of single crystal magnetisation between 4–0.1 K (Neiheisel *et al* 1975). A fit of their data on the dimer model for effective spin $S = 1/2$ ($M_s = 1/2$ lying lowest, D positive) gave a value of $J = -0.07 \text{ cm}^{-1}$. The magnetic interaction is, as expected, weak and antiferromagnetic. If this value of exchange interaction is included in the theoretical fitting, $D = 6.0 \text{ cm}^{-1}$ fits the magnetisation data of figure 5 well.

Fe(PP)Cl and Fe(DPDME)Cl: The single crystal structural data on Fe(PP)Cl, which is also called hemin chloride, show that the molecule has a stereochemical structure closely related to the Fe(TPP)X series. The iron is slightly out of the plane of the porphyrin core and is coordinated to the chlorine atom completing an approximate square pyramidal geometry around it. Relevant structural data are included in table 1. Though no structural data are available for Fe(DPDME)Cl, the

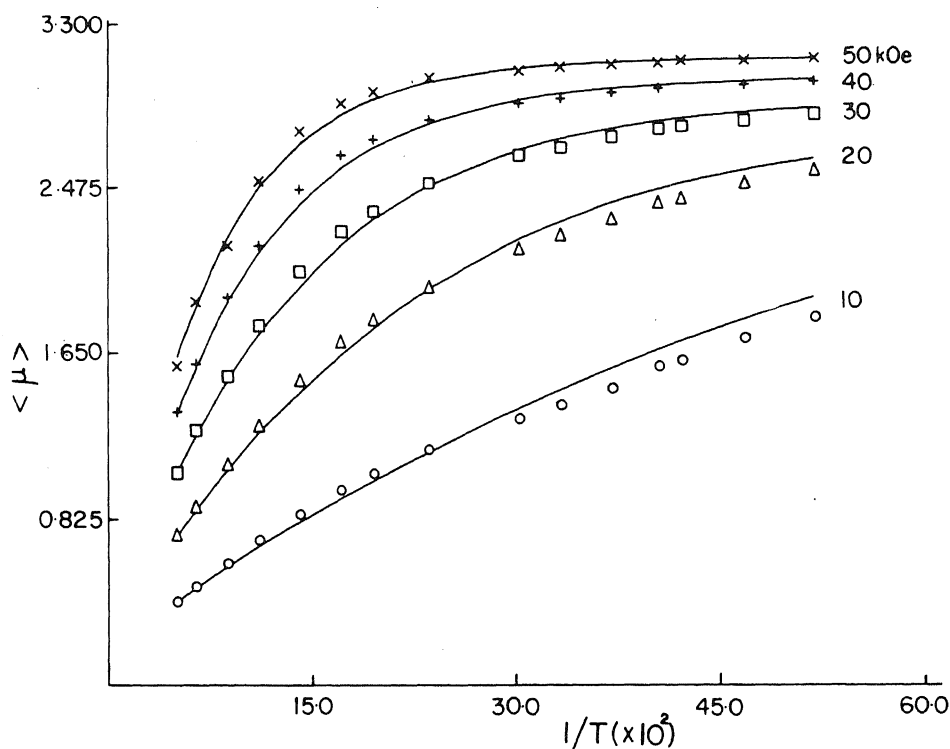


Figure 6. Magnetisation of Fe(TPP)Br down to 2 K (Behere *et al* 1979). Solid curves are calculated for $D = 12.5 \text{ cm}^{-1}$.

Table 1. Magnetic and structural parameters for some high-spin iron(III) porphyrins.

Compound	Fe-X (Å)	Fe-N (Å)	Fe-Ct (Å)	$\langle \mu \rangle_{\text{sat}}$ (BM)	D (cm^{-1})	ZJ (cm^{-1})	Remarks
Fe(TPP)Cl	2.192	2.060	0.39	3.4	8.0 ^a 6.0 ^{a,b}	— -0.07	Exchange not considered Exchange included with $Z = 2$ (dimer model)
Fe(TPP)Br	2.348	2.069	0.56	3.0	12.5 ^{a,b}	—	Inclusion of exchange not considered important
Fe(PP)Cl	—	—	0.49	3.4	8.0 6.95 ^c	— -0.08	Exchange not considered Molecular field model
Fe(DPDME)Cl	—	—	—	3.0	11.0 9.0 ^c	-0.22 —	Molecular field model Far infrared measurement

^a From magnetisation; ^b value derived from single crystal studies as well; ^c far infrared measurement.

stereochemical structure is expected to be similar to the above five-coordinated high-spin iron(III) porphyrins. The temperature dependence of the effective

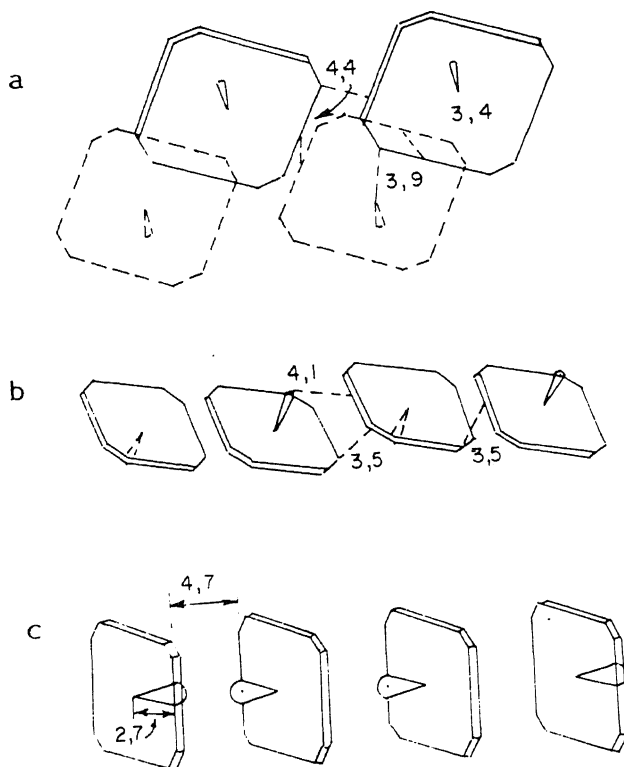


Figure 7. Molecular stacking in some iron(III) porphyrins: (a) Fe(PP)Cl; (b) Fe(DEP); (c) Fe(TPP)Cl.

average magnetic moment of these complexes is shown in figure 8. While the general nature of the $\bar{\mu}_{\text{eff}}$ vs T curves is similar to that of Fe(TPP)X, the magnetic moment of Fe(DPDME)Cl decreases much faster than that of Fe(TPP)X. For example the $\bar{\mu}_{\text{eff}}$ for the deuterio complex at 4.2 K is 4.2 BM as against 4.6 BM for Fe(PP)Cl, 4.8 BM for Fe(TPP)Cl and 4.5 BM for Fe(TPP)Br. The large decrease in the $\bar{\mu}_{\text{eff}}$ for the deuterio complex may arise from a much larger D -value or presence of large antiferromagnetic exchange interaction.

The magnetisation of these two molecules has been reported between 2–20 K and 10–50 kOe (Marathe and Mitra 1983) and is summarised in figures 9 and 10. The general features of the magnetisation of the two compounds are similar to those of Fe(TPP)X. In both the molecules the magnetisation saturates below 4 K for $H \geq 40$ kOe. The saturation moment for the Fe(DPDME)Cl is however much lower than that of the Fe(PP)Cl (see table 1).

Equation (1) gave excellent fit to the $\langle \mu \rangle$ vs $1/T$ (and $\bar{\mu}_{\text{eff}}$ vs T as well) data for the Fe(PP)Cl over the entire temperature and magnetic field range for $D = 8.0 \text{ cm}^{-1}$. The value of D in Fe(PP)Cl has however been accurately determined by far infrared spectroscopy (Brackett *et al* 1971) which has yielded $D = 6.95 \text{ cm}^{-1}$. The discrepancy may not be large but is significant. A similar attempt to fit the data for Fe(DPDME)Cl was however unsuccessful. The $\bar{\mu}_{\text{eff}}$ vs T data could only be fitted to $D = 30 \text{ cm}^{-1}$ which is unreasonably high. The

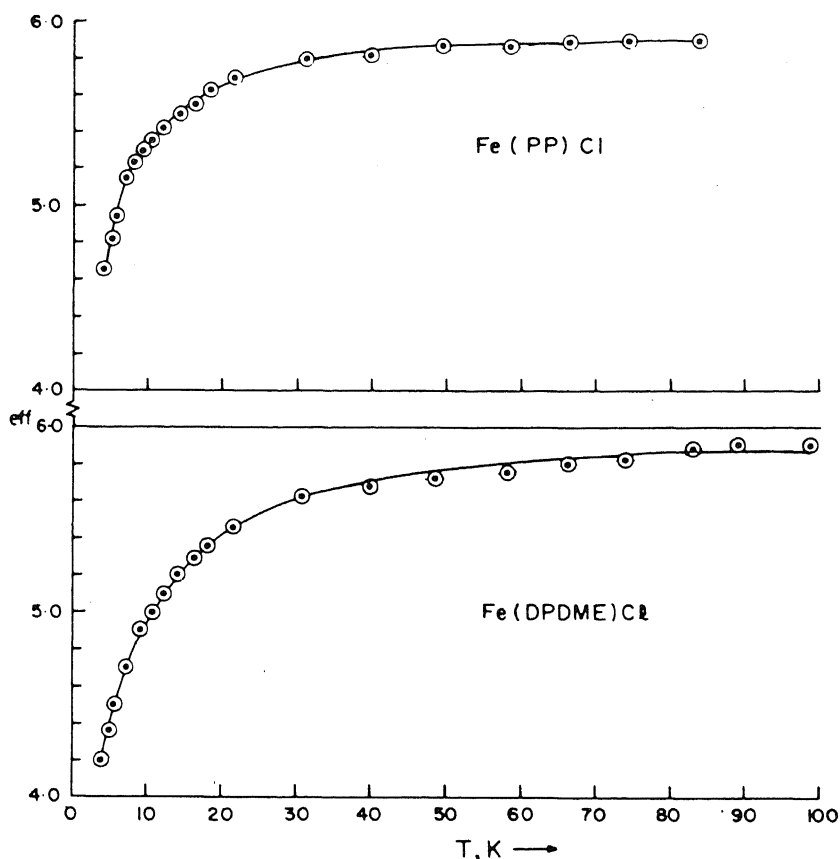


Figure 8. Temperature dependence of $\bar{\mu}_{\text{eff}}$ for Fe(PP)Cl and Fe(DPDME)Cl (Marathe and Mitra 1983).

magnetisation data over the entire range of magnetic fields could not be fitted at all to any single value of D . While the lower field data ($H \leq 20$ kOe) can only be fitted to an unreasonably high value of D (~ 30 – 25 cm^{-1}), the 50 kOe data can be fitted to $D = 11.0$ cm^{-1} . The data at intermediate magnetic fields correspond best to values of D lying between 11.0 and 30.0 cm^{-1} . The D value of Fe(DPDME)Cl is also known accurately from the far infrared spectroscopy, giving $D = 9.0$ cm^{-1} (Brackett *et al* 1971).

It has been suggested that the above discrepancies indicate the presence of significant magnetic exchange interaction between the ferric ions in the crystal lattice (Marathe and Mitra 1983). To explain the magnetisation the exchange interaction must be included in (1). In view of the uncertainty in the structure of the Fe(DPDME)Cl it is appropriate to consider the exchange interaction in a general way in molecular field framework. Equation (1) may then be modified, above the Neel temperature, as (Marathe and Mitra 1983),

$$H_s = DS_z^2 + g\beta H.S - 2ZJ\langle S \rangle S. \quad (2)$$

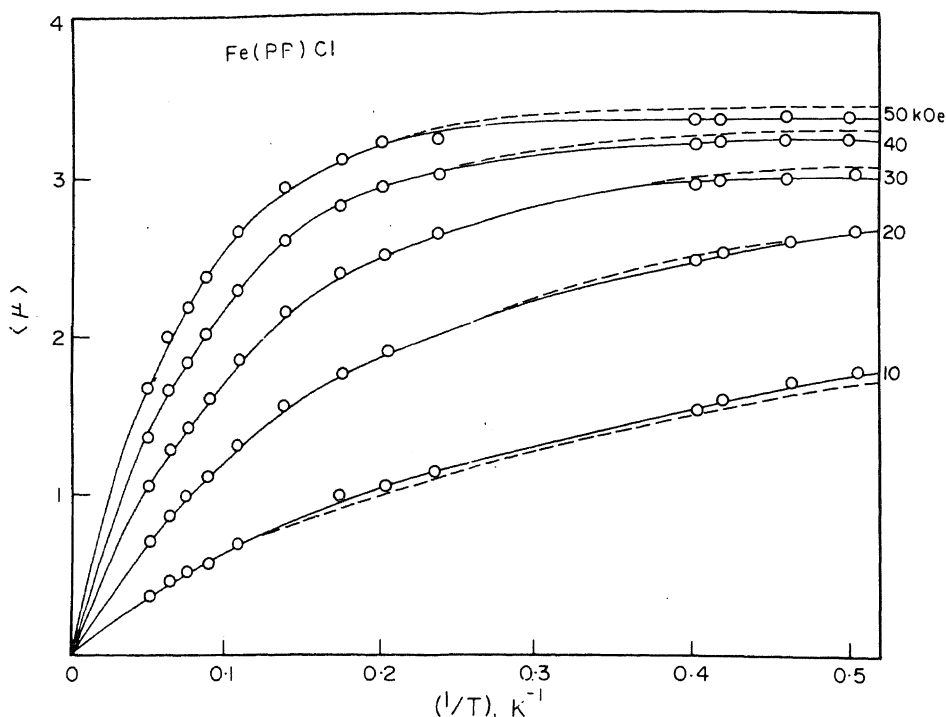


Figure 9. Magnetisation of Fe(PP)Cl down to 2 K (Marathe and Mitra 1983). The solid curves are for $D = 8.5 \text{ cm}^{-1}$ without exchange interaction. The broken curves are calculated for $D = 6.95$ and $ZJ = -0.08 \text{ cm}^{-1}$.

Here Z is the number of nearest equivalent neighbours interacting with an exchange interaction J , and $\langle S \rangle$ is the expectation value of the spin operator S given by the relation

$$\langle S \rangle = \frac{\sum_i \exp(-E_i/kT)}{\sum_i} \langle \psi_i | S | \psi_i \rangle \exp(-E_i/kT),$$

where E_i and ψ_i are the eigenvalues and eigenvectors of the spin Hamiltonian H_s in (2). Since the value of $\langle S \rangle$ depends on the H_s which contains $\langle S \rangle$, an iterative procedure was used to calculate $\langle S \rangle$ self-consistently. Using this procedure magnetisation has been calculated as a function of temperature and magnetic field to fit the entire set of data for Fe(PP)Cl and Fe(DPDME)Cl (Marathe and Mitra 1983). The best fit values are listed in table 1. It is encouraging to find that with the inclusion of the exchange interaction the fit to the data is very good over the entire range of temperature and magnetic field, especially so, for Fe(DPDME)Cl (see figures 9 and 10). The exchange energy is small, as expected; however, for deuteroporphyrin it is three times larger than that for hemin chloride. Further the discrepancy mentioned above in the value of D for hemin chloride disappears when even a very weak exchange interaction is included in fitting the data.

The existence of weak exchange interaction in these and other metalloporphyrins is interesting. Since these molecules are relatively large and do not possess a polynuclear structure, they were considered to be magnetically dilute. This does not seem to be true at very low temperatures. A further point of interest is that the magnetisation data at different fields are more sensitive to weak exchange interaction and hence better suited for its detection and evaluation.

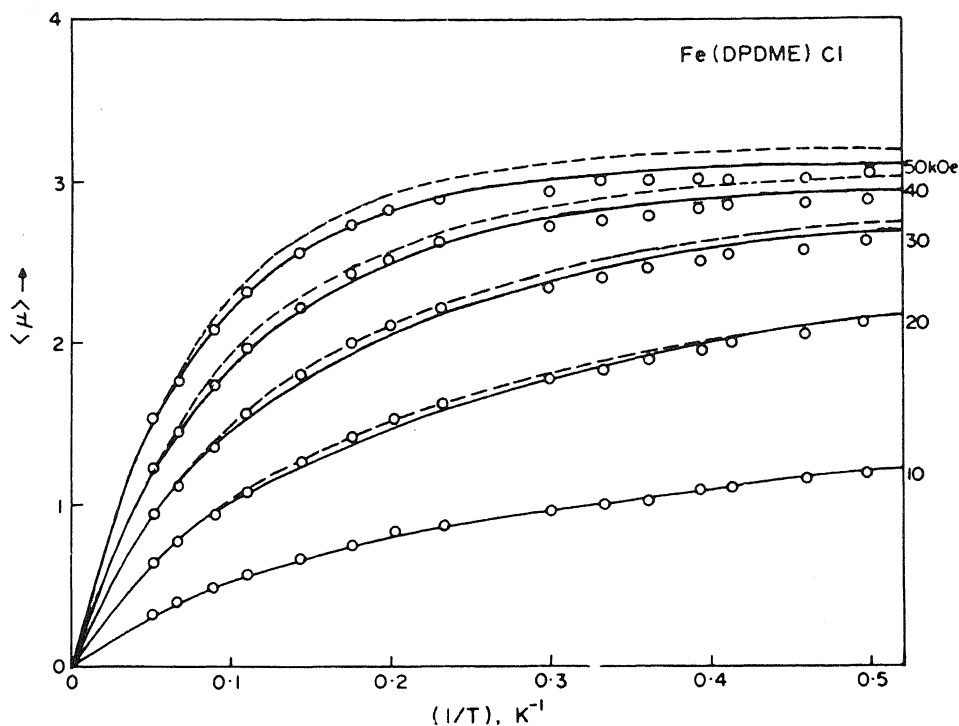


Figure 10. Magnetisation of Fe(DPDME)Cl down to 2 K (Marathe and Mitra 1983). The solid and broken curves are calculated ones for $D = 11.0$ and $ZJ = -0.22 \text{ cm}^{-1}$, and $D = 9.0$ and $ZJ = -0.20 \text{ cm}^{-1}$ respectively.

4.2 High-spin manganese(III) porphyrins

Manganese(III) porphyrins are usually high-spin ($S = 2$) with 5B_1 ground state. The combined effect of spin-orbit coupling and the axial crystal field partly removes the spin-degeneracy as shown in figure 11. Here D is positive when $M_s = 0$ lies lowest, negative when $M_s = \pm 2$ of the lowest. The magnetic properties of the manganese(III) porphyrins are, as in iron(III) porphyrins, largely governed by the sign and magnitude of the zero-field splitting.

Magnetisation of several manganese(III) porphyrins has been reported over a wide range of temperature and magnetic fields. The measurements on Mn(TPP)Cl and Mn(TPP)Cl(py) extend between 2–20 K and 10–50 kOe, and show complete saturation of the magnetisation (Behere *et al* 1981b). Magnetisation measurements on Mn(TPP)OAc.H₂O and Mn(OEP)ClO₄.H₂O also extend over a wide range of magnetic fields and temperatures (upto 4 K) but do not show complete saturation (Kennedy and Murray 1985). Limited measurements on some other manganese(III) porphyrins have also been recently reported (Dugad *et al* 1984). We discuss below some of these results in detail.

Mn(TPP)Cl and *Mn(TPP)Cl(py)*: Complete structural data on these two compounds are available (Tulinsky and Chen 1977; Kirner and Scheidt 1975). In *Mn(TPP)Cl* the manganese atom has a square pyramidal structure as in *Fe(TPP)Cl* with the manganese atom being coordinated to four basal pyrrole nitrogens and an axial chloride ion. In *Mn(TPP)Cl(py)* hexacoordinated geometry is completed by the pyridine through a long $M-N_{py}$ bond. Some relevant structural data are

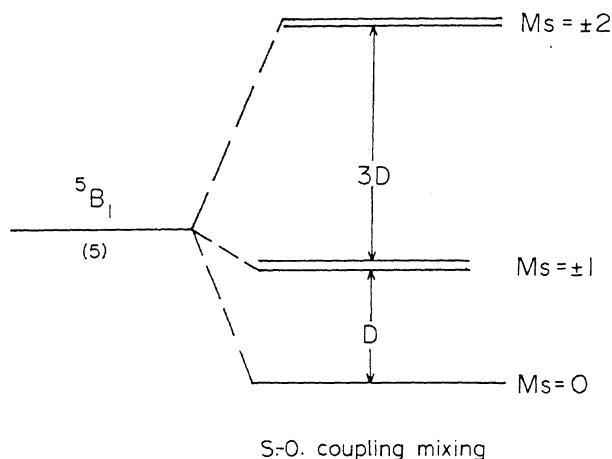


Figure 11. Zero field splitting in manganese(III) porphyrins (d^4 electron configuration).

Table 2. Magnetic and structural parameters for some high-spin manganese(III) porphyrins.

Compound	Fe-X	Fe-N	Fe-Cl	$\langle\mu\rangle_{sat}$	D	ZJ	Remarks
<i>Mn(TPP)Cl</i>	2.373	2.008	0.27	3.44	-2.3	—	From high temperature single crystal measurement
					-1.9	-0.25	Exchange included with <i>MF</i> model
<i>Mn(TPP)Cl(py)</i>	2.468	2.009	0.12	3.01	-3.0	—	From high temperature single crystal measurement
					-3.0	—	From magnetisation measurement
<i>Mn(OEP)OAc</i>	—	—	—	3.0	-1.9	—	Value deduced from magnetisation
<i>Mn(OEP)ClO₄</i>	—	—	—	2.7	-2.3	$J = -0.07$	Deduced from magnetisation
<i>Mn(TPP)ClO₄</i>	—	—	—	—	-2.0	—	From μ_{eff} vs T data
<i>Mn(TPP)(1-MeIm)₂ClO₄</i>	—	—	—	—	-2.5	—	From μ_{eff} vs T data

included in table 2. The effective average magnetic moment of these two compounds is nearly constant at 4.9 BM down to about 20 K below which it decreases sharply (figure 12) (Behere and Mitra 1980). The decrease is similar to that observed in high-spin iron(III) porphyrins and has been largely ascribed to zero-field splitting. The magnetisation data are also very similar to those on Fe(TPP)X (figures 13 and 14). The moments saturate at 3.44 and 3.01 BM for the chloro and the pyridinato compounds. The higher saturation moment for the chloro compound suggests, on simple consideration, a lower zero-field splitting. This is consistent with the $\bar{\mu}_{\text{eff}}$ vs T data in figure 12 which shows that the variation in $\bar{\mu}_{\text{eff}}$ with temperature for the Mn(TPP)Cl is much less. The saturation moments in both the compounds are however much less than $\langle\mu\rangle_{\text{sat}} = 4.0$ BM expected from the Brillouin function for $S = 2$ and $g = 2$ (see figure 1), and reflect the effect of zero-field splitting of the ground state.

The sign and magnitude of the zero-field splitting in these manganese(III) porphyrins has been accurately determined by single crystal magnetic susceptibility

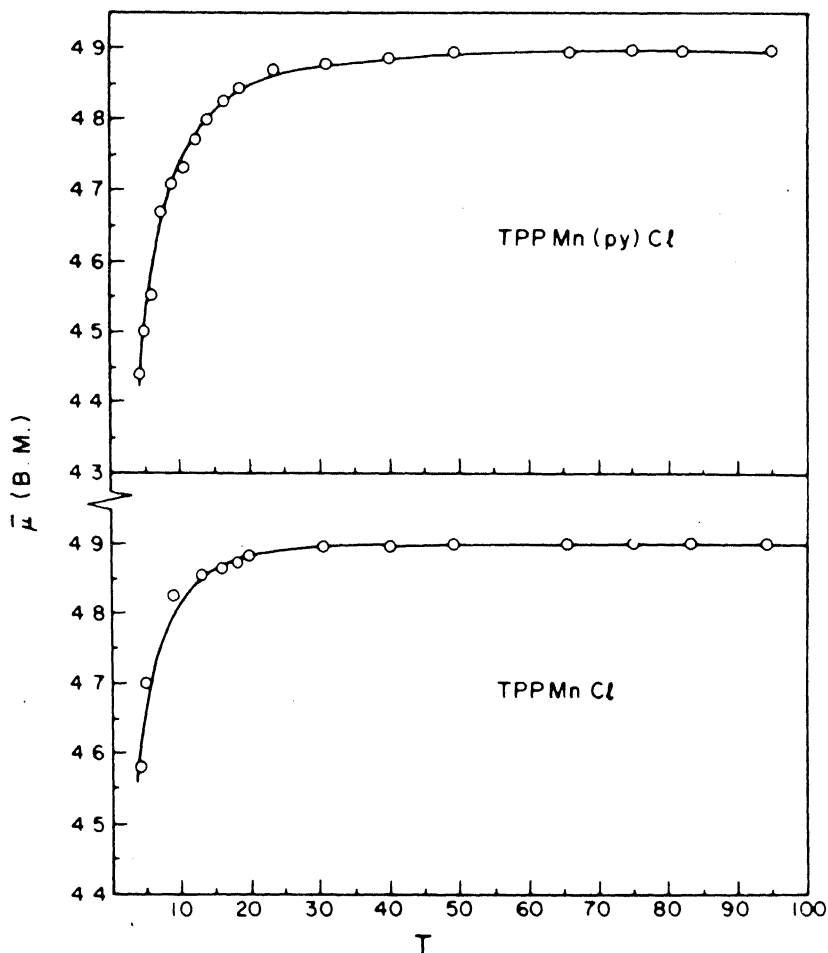


Figure 12. Temperature dependence of $\bar{\mu}_{\text{eff}}$ for Mn(TPP)Cl and Mn(TPP)(py)Cl.

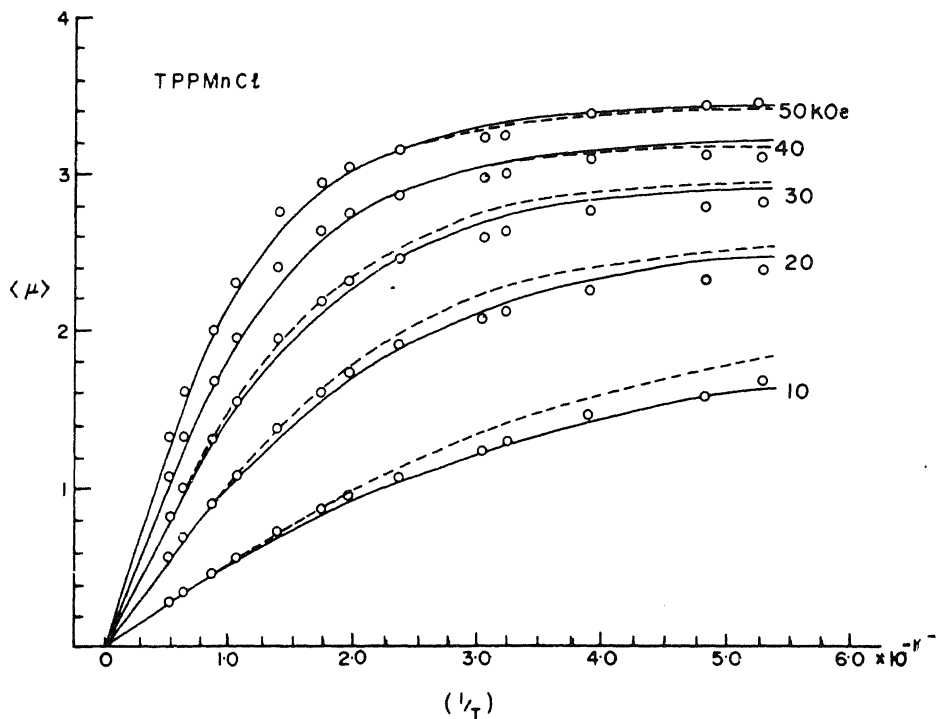


Figure 13. Magnetisation data on Mn(TPP)Cl(py) between 20–2 K (Behere *et al* 1981b). Solid curves are theoretical fits for $D = -3.0 \text{ cm}^{-1}$.

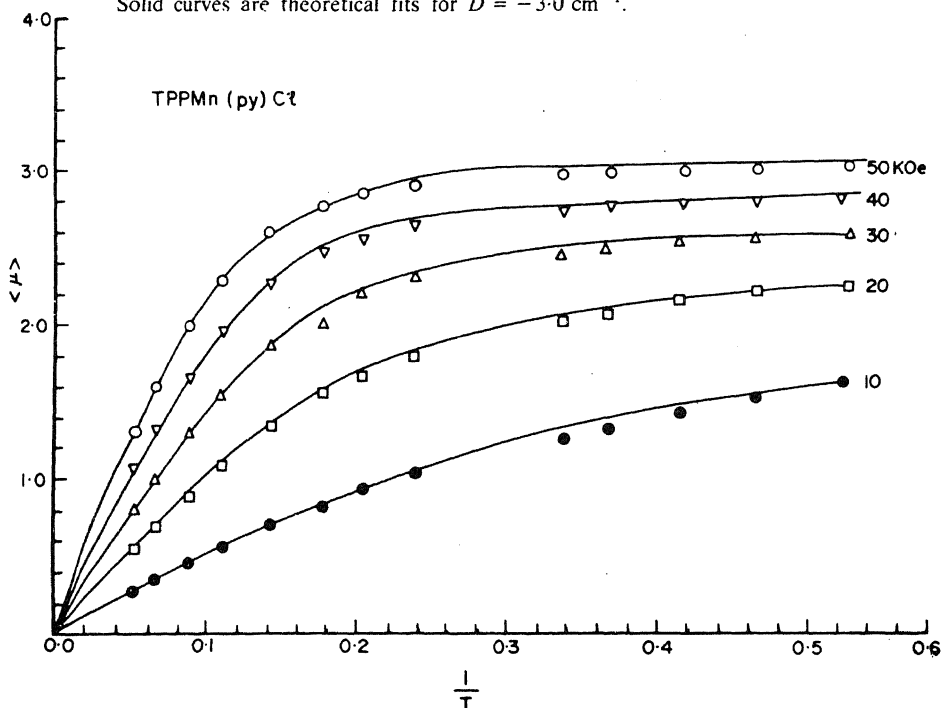


Figure 14. Magnetisation data on Mn(TPP)Cl between 20 and 2 K. The broken and solid curves are theoretical fits without and with exchange interaction (Behere *et al* 1981b).

measurements (Behere and Mitra 1980b). These values are included in table 2. Using (1) the magnetisation was fitted by varying D . Excellent agreement was obtained for $\text{Mn}(\text{TPP})\text{Cl}(\text{py})$ for $D = -3.0 \text{ cm}^{-1}$, but for $\text{Mn}(\text{TPP})\text{Cl}$ no fit was possible for any value of D over the entire range of temperature and magnetic fields. As in the case of $\text{Fe}(\text{DPDME})\text{Cl}$, presence of magnetic exchange was considered as the reason for this discrepancy. Including magnetic exchange within molecular field approximation, (2) gave excellent fit to the data for $\text{Mn}(\text{TPP})\text{Cl}$ for $D = -2.3 \pm 0.5 \text{ cm}^{-1}$ and $JZ = -0.025 \text{ cm}^{-1}$.

The values of D obtained from the magnetisation agree well with the single crystal values (table 2). The D is negative and small as against the large positive values for the iron(III) porphyrins. The origin of the negative sign and small magnitude of D in manganese(III) porphyrins has recently been explained on a crystal field theory (Dugad *et al* 1984).

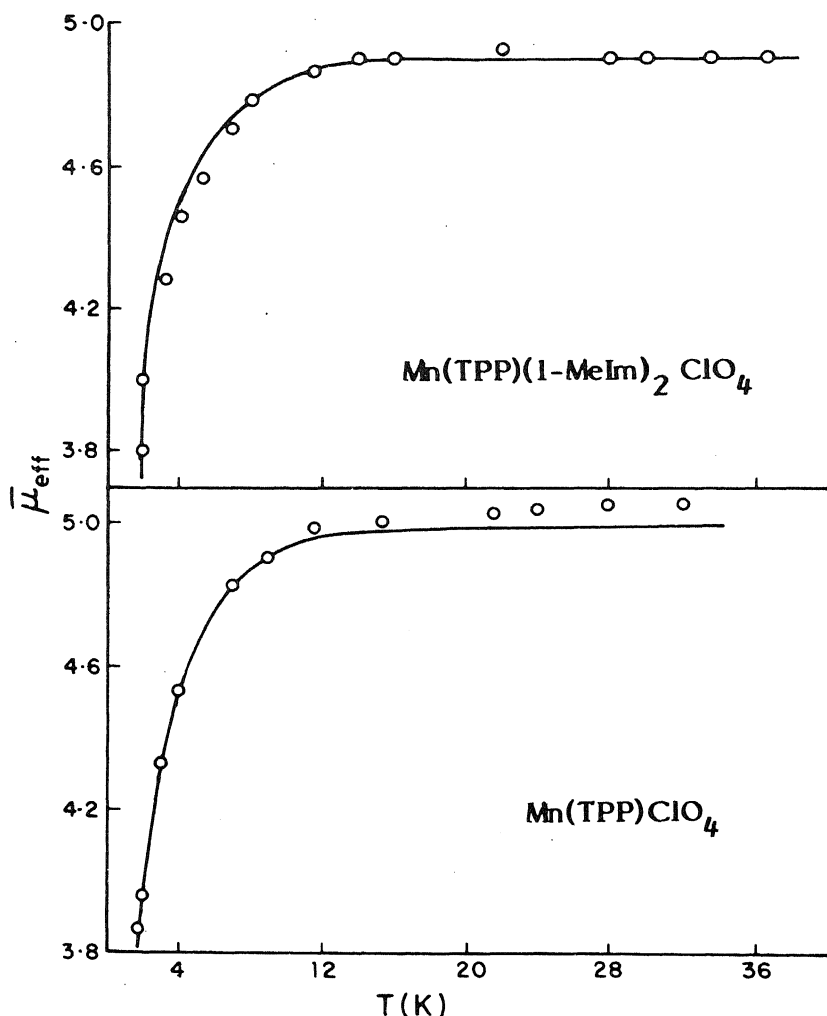


Figure 15. Temperature dependence of μ_{eff} for $\text{Mn}(\text{TPP})\text{ClO}_4$ and $\text{Mn}(\text{TPP})(1\text{-MeIm})_2\text{ClO}_4$ (Dugad *et al* 1984).

Mn(TPP)ClO₄ and Mn(TPP)(ClO₄)(1-MeIm)₂: Mn(TPP)ClO₄ is structurally analogous (Reed *et al* 1978) to Fe(TPP)ClO₄ which shows novel spin-mixed ground state between $S = 5/2$ and $3/2$ (Mitra *et al* 1983). Mn(TPP)ClO₄ (1-MeIm)₂ is hexacoordinated and similar ferric porphyrins are known to be low-spin (Scheidt and Gouterman 1983). Magnetic measurements on these two molecules between 2–100 K and upto 15 kOe at 4.2 K (Dugad *et al* 1984) establish them to be strictly high-spin with values of D similar to other manganese(III) porphyrins (figure 15; table 2). The effect of axial perchlorate coordination in manganese(III) porphyrins appears to be thus minimal, in contrast to the dramatic effect it has on the iron(III) porphyrins, where it changes the spin state of the metal ion.

Mn(TPP)(Cl,Br)H₂O and Mn(OEP)OAc.H₂O: Magnetisation of several of the manganese(III) porphyrins of general formula Mn(Porph)X.L where X = Cl, Br, OAc, ClO₄ and L = H₂O has been reported between 4.2–25 K and 5–46 kOe (Kennedy and Murray 1985). Though the moments do not reach saturation at the lowest temperature and highest field of measurement, the data are adequate to derive values of D . In all cases a small exchange interaction was found to be present. The values of D fall within the range of other manganese(III) porphyrins (table 2).

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Spin glass behavior in some ternary metal chalcogens

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Abstract. The magnetic properties of some amorphous metallic materials of the formula M_2SnTe_4 , where $M = Cr, Mn, \text{ and } Fe$, are presented. The materials exhibit anomalous magnetic behavior at low temperatures. The field cooled and zero field cooled d.c. magnetic susceptibilities show different behavior when measured below the transition temperature. The materials exhibit a thermal remanent magnetization and isothermal remanent magnetization that is consistent with that of a spin glass. The spin glass freezing temperatures for these materials are 18 K, 11 K, and 12 K for $M = Cr, Mn, \text{ and } Fe$, respectively.

Keywords. Spin glass behavior; ternary metal chalcogens; magnetic properties, amorphous metallic substances.

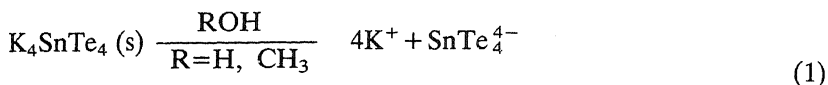
1. Introduction

In two previous communications, we described the synthesis and characterization of a series of ternary metal chalcogens of the formula M_2SnTe_4 where $M = Cr, Mn, Fe, \text{ and } Co$ (Haushalter *et al* 1984a,b). The zero field variable temperature electrical conductivities of these materials have also been studied (Goshorn *et al* 1986). These new materials exhibit some remarkable properties including resistivity ranging from 10^4 to 10^{-4} (ohm-cm), a spin glass "transition" at temperatures ranging from 5 to 18K, and amorphous structure down to the $10\text{\AA}$ level. In addition, some novel reactions of the precursor ternary Zintl phase materials with polyimide plastics have been described (Haushalter 1983; Haushalter and Krauss 1983).

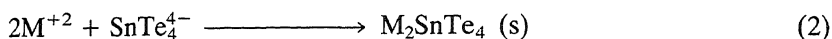
The preparation of the ternary metal chalcogens involves a metathesis reaction between a Zintl phase material (K_4SnTe_4) and a divalent transition metal bromide. The Zintl phase results from the interaction between the less electronegative metals (i.e., alkali and alkaline earth metals) and the more electronegative metals and metalloids (i.e., the post-transition metals). There are several reviews that describe the properties of the Zintl phase materials (see for example, Shafer *et al* 1973; Corbett 1985). The Zintl phase of matter can be described as a polar metallic alloy in which the bonds have a substantial amount of ionic character. The ionic character of the Zintl phase is often sufficient to allow for the solvation of salt-like ions in polar solvents (e.g., KSn dissolves in liquid NH_3 and K_4SnTe_4 dissolves in H_2O).

The transition metal tin tellurides are prepared from the Zintl phase material K_4SnTe_4 . The ionic character of K_4SnTe_4 permits the Zintl phase alloy to form an aqueous ionic solution as shown in (1).

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This material is quite reactive and, in the presence of a metal cation of sufficient electron affinity, will form an insoluble metallic alloy of formula M_2SnTe_4 due to the transfer of electrons from the SnTe_4^{4-} ion to the metal following reaction (2).



X-ray powder diffraction patterns exhibit a lack of long range crystalline order for the freshly prepared material. Subsequent neutron diffraction verified the glassy amorphous nature of the materials. Since these materials show a tendency to decompose at higher temperatures (*vide infra*), high temperature techniques such as rapid thermal quenching could not be used to produce these amorphous materials. Also sputtering techniques would not be expected to generate the SnTe_4 tetrahedra.

The first clue to the unusual magnetic properties of these materials came from the Mossbauer experiment (Haushalter *et al* 1984b). These experiments revealed the presence of a large moment in the freshly prepared material at low temperature resulting from ordered spins on both the iron and the tin atoms. This implies that the electrons are somewhat delocalized. Magnetic susceptibility experiments verified the existence of the spin glass state in these materials.

Over the past fifteen years, the spin glass phenomenon has grown into a sizable area of research in solid state science (see, for example, Moorjani and Corey 1985; Edwards and Anderson 1975, 1976; Fisher 1983, 1985). The spin glass problem provides a testing ground for the theories that attempt to address many intriguing questions concerning amorphous structure and magnetism, the nature of the spin glass state, and the relation of the spin glass transition to critical phenomena.

There are several reviews that discuss the theory, and concept of the spin glass phenomenon, as well as the many reports of experimental studies on spin glasses (for a recent review see, Moorjani and Corey 1985; or Fisher 1983, 1985). The spin glass phenomenon first came to prominence following reports by Mydosh and coworkers that a cusp in the AC susceptibility of AuFe was observed at a well-defined temperature (Cannella *et al* 1971). These initial reports did not mention a frequency dependence of the temperature of the cusp in the susceptibility and it was thought a phase transition to a new state had occurred (Edwards and Anderson 1975). However, subsequent reports on other complexes showed a significant dependence of peak height and temperature on the ac frequency.

Another curious feature of spin glass systems is the marked difference between the AC and DC susceptibility. The DC susceptibility is very dependent on the manner in which the experiment is performed (Guy 1979). For example, a zero field cooled specimen shows very different behavior from a field cooled specimen, and even the rate of cooling of a field cooled sample has an effect on the response of the sample to a DC susceptibility measurement below the spin glass temperature. These observations are inconsistent with the usual concept of phase transition. In addition to the curious magnetic behavior, other experiments, for example heat capacity (Wenger and Keesom 1975, 1976) and conductance

(Laborde and Radakrishna 1973; Ford and Mydosh 1980), were also difficult to reconcile to a phase transition model. As a result, the term "spin glass" was coined to describe the emerging magnetic effects that had an uncanny resemblance to the behavior observed in real glass systems. Current theories are again developing that support the phase transition model, but there is still a great deal of speculation and controversy over whether an equilibrium state even exists (see for example Fisher 1985; Souletie 1985).

In this report, we describe the d.c. magnetic susceptibility and remanent magnetization experiments on the complexes M_2SnTe_4 , where $M = Cr, Mn, Fe$. These complexes exhibit properties consistent with the spin glass state. The spin glass freezing temperatures are in the range 12–18 K.

2. Experimental

Syntheses: All of the materials are extremely air sensitive. Preparation and sample manipulations were performed under an argon atmosphere.

K_4SnTe_4 : The ternary Zintl material K_4SnTe_4 was prepared as described earlier (Huffman *et al* 1984).

M_2SnTe_4 : Methanolic solutions containing a stoichiometric amount of the transition metal bromides were mixed with methanolic solutions of K_4SnTe_4 and the product material M_2SnTe_4 immediately formed as a metallic black precipitate. The black precipitate was filtered, washed with ethanol, and dried in vacuum overnight.

Magnetic measurements: Variable temperature magnetization measurements were recorded on a SHE Corporation Superconducting SQUID susceptometer. Measurement and calibration techniques are reported elsewhere (O'Connor 1982).

3. Results and discussion

The d.c. magnetic susceptibility of each of the samples deviated greatly from Curie-Weiss behavior. At the lowest temperatures, the magnetic data of these materials exhibited anomalous magnetic behavior consistent with a magnetic phase transition. The spin glass character of the material became evident when different environments of sample cooling were used.

Figure 1 illustrates the low temperature d.c. magnetic susceptibility for Mn_2SnTe_4 . Two experiments are included in this plot. First the sample was cooled in a magnetic field ($H_c = 10$ mT) and then measured in the same field ($H_m = 10$ mT). The magnetic data are plotted as a function of temperature up to 100 K. The inset shows the magnetic response of the sample when it is cooled in a zero magnetic field ($H_c = 0$) and then measured in an applied magnetic field ($H_c = 10$ mT). Difference in these data sets is expected for a material with a spin glass transition at a freezing temperature $T_f \approx 12$ K.

The iron and chromium analogs also exhibit this phenomenon. For example, figure 2 shows the magnetic response of Fe_2SnTe_4 over the 5 to 20 K temperature region. In these experiments, the same measuring field ($H_m = 10$ mT) is again used. For one data set the sample was cooled in a zero magnetic field ($H_c = 0$) and

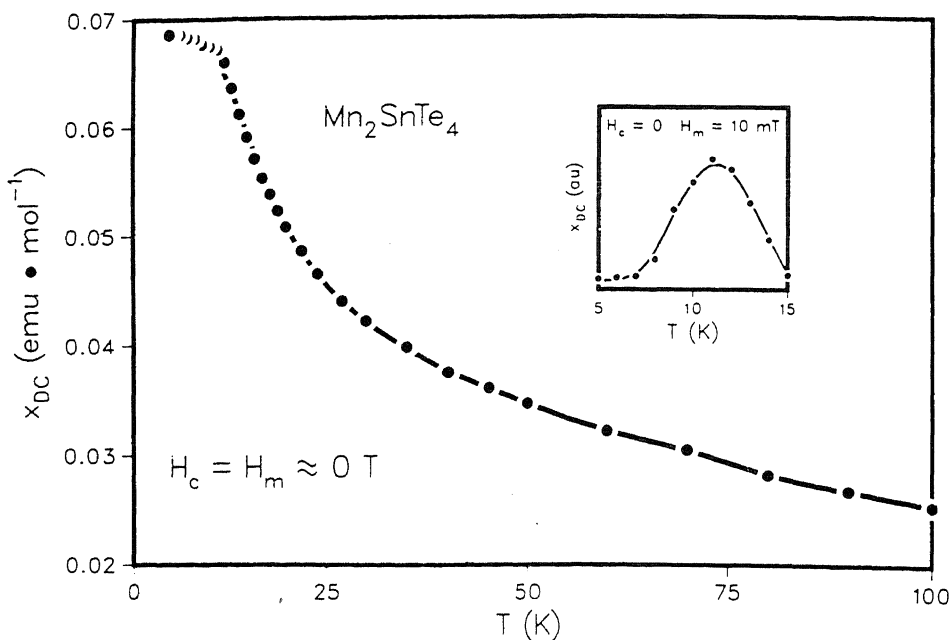


Figure 1. A plot of the d.c. magnetic susceptibility of Mn_2SnTe_4 . The sample was frozen and measured in a field of 10 mT. The inset illustrates the magnetic response of a sample frozen at zero field and then measured at 10 mT.

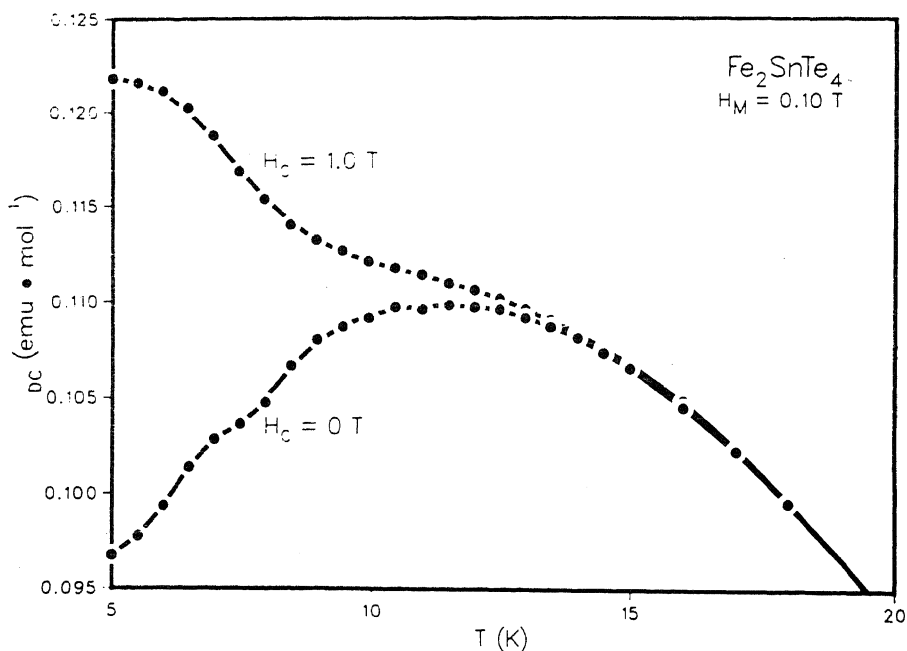


Figure 2. A plot of the magnetic susceptibility as a function of temperature for Cr_2SnTe_4 . The two curves at low temperature illustrate the effect of zero field cooling (lower curve) and high field (1.0 T) cooling (upper curve). The two curves merge in the paramagnetic domain above the spin glass freezing temperature.

for the other data set the sample was cooled in a large magnetic field ($H_c = 1$ T). When the spin glass is cooled in a zero field, the spins are frozen in a random orientation. The spins try and maintain their random frozen alignment when the measuring field is turned on. As the spin glass freezing temperature is passed, the spins begin to "melt" and the paramagnetic phase is entered.

When the spin glass is cooled in a large applied field ($H_c = 1.0$ T), the spins freeze in alignment with the applied magnetic field. The frozen spins try to maintain this alignment even when the field is reduced. This results in a measured d.c. susceptibility that is larger than the value measured for the zero field cooled specimen. At temperatures above the spin glass freezing temperature, there is no difference between the magnetic response for each of the cooling experiments.

The spin glass freezing temperatures are listed in table 1 for the complexes M_2SnTe_4 , where $M = Cr, Mn$, and Fe . Also listed in table 1 are the conductivities and standard reduction potentials for these materials. The degree of metallic character (conductivity) appears to show some correlation with the reduction potential of the metal ions in solution (Goshorn *et al* 1986). This correlation is not as striking for the spin glass freezing temperatures but does show a general trend. A better correlation should be apparent upon a comparison of electron affinities in the solid state. For comparison, the oxidation potential of $SnTe_4^{4-}$ has been estimated by chemical means to be 0.7 ± 0.2 V.

There are three general approaches to describing the spin glass phenomenon. The first general approach is the Néel description. This is an analogy with superparamagnetism in which domains of random moments are connected by free spins. A thermodynamic blocking equilibrium is then achieved via a mechanism called the RKKY interaction, and a random locking of the moments occurs at T_f . The second approach to understanding the spin glass phenomenon proposes a regular lattice of spins with random degrees of coupling forces, usually a Gaussian probability of interaction strengths. The most attractive feature of this model is the simplicity of the theory and its lending itself to the calculation of critical exponents. The third approach is the "window glass" analogy to the freezing of structural glasses. This analogy gave rise to the term spin glass and is consistent with many of the properties observed. This model does not predict a distinct phase transition but rather a gradual change in the viscosity of the spins as the moments are less able to follow an external magnetic field. The major advantage of this approach is that it is very easy to grasp the concept of the spin glass on an intuitive level. Although some of the predictions of these theories occasionally agree, the theories often contradict

Table 1. List of standard reduction potentials ($M^{+2} + 2e^- \longrightarrow M$), resistivity (ρ), and spin glass freezing temperatures for M_2SnTe_4 , $M = Cr, Mn$ and Fe .

M	E° (volts)	ρ (ohm cm)	T_f (K)
Cr	-0.559	-	18
Mn	-1.029	3×10^4	11
Fe	-0.409	9×10^{-4}	12

one another and each has serious shortcomings in its ability to explain all the facts of the spin glass state.

The spin glass phenomenon is characterized by some very unusual behavior in the bulk magnetic properties of the materials. The electrons ability to follow a magnetic field is drastically modified by the onset of the spin glass state. The freezing of the moments can result in a large remanent magnetization in the material. Perhaps the most diagnostic experiment for the characterization of the spin glass state is the analysis of the field dependence of the isothermal remanent magnetization and thermal remanent magnetization.

Isothermal remanent magnetization (IRM): This experiment involves cooling the specimen in a zero field to temperatures below the spin glass freezing point. The onset of the spin glass phase then results in a freezing of the magnetic moments in a truly random fashion since no external force was present for the spins to align with. The specimen is then exposed to an applied magnetic field. After a certain time, the applied field is quenched and the resultant magnetization is measured in zero applied magnetic field. Under these conditions an ideal spin glass would show zero magnetization since the spins would remain frozen randomly throughout the bulk of the specimen.

Thermal remanent magnetization (TRM): This experiment on the other hand exhibits vastly different magnetic behavior. In the TRM experiment, the specimen is cooled to a temperature below the spin glass freezing temperature while in an applied magnetic field. The spins, which had a tendency to align with the applied magnetic field while in the paramagnetic phase, are now frozen into a position of partial alignment with the applied field. While the specimen is in the frozen spin glass state, the magnetic field is quenched. Since the spins are frozen, their alignment is not quenched and a resultant moment is present in the material. The TRM measurement should give a large remanent relative to the IRM.

The TRM, IRM experiment for Cr_2SnTe_4 is illustrated in figure 3. The hump in the TRM curve has been observed in many spin glasses and is characteristic of the spin glass state; nevertheless, this anomaly escapes theoretical explanation. The two curves begin to converge at fields near 1.0 T indicating that the spin glass state is destroyed by high fields.

The effect of the TRM is greatly enhanced by performing the experiment at lower temperatures. Figure 4 illustrates a plot of $\ln \text{TRM}$ as a function of temperature. In TRM values of -3 are negligible and may be assumed to represent the absence of a magnetic remanence. This indicates that the paramagnetic phase dominates.

Another important property of spin glasses is their time dependence. A log/log plot of the TRM of Fe_2SnTe_4 as a function of the time exhibits a straight line. The initial thermal remanent magnetization is therefore transient because of a large reversible component. But the TRM then begins to approach a quasi-steady state value after a few minutes. Figure 5 illustrates this behavior for Fe_2SnTe_4 .

The RKKY interaction, bond disorder, topological disorder, and impurity centers are all candidates for the source of the frustration that is necessary for the spin glass state to exist. The RKKY interaction is the primary cause of frustration in conducting amorphous materials such as the dilute noble metal alloys. The phase dependence of the interaction causes the frustration necessary for blocked spin

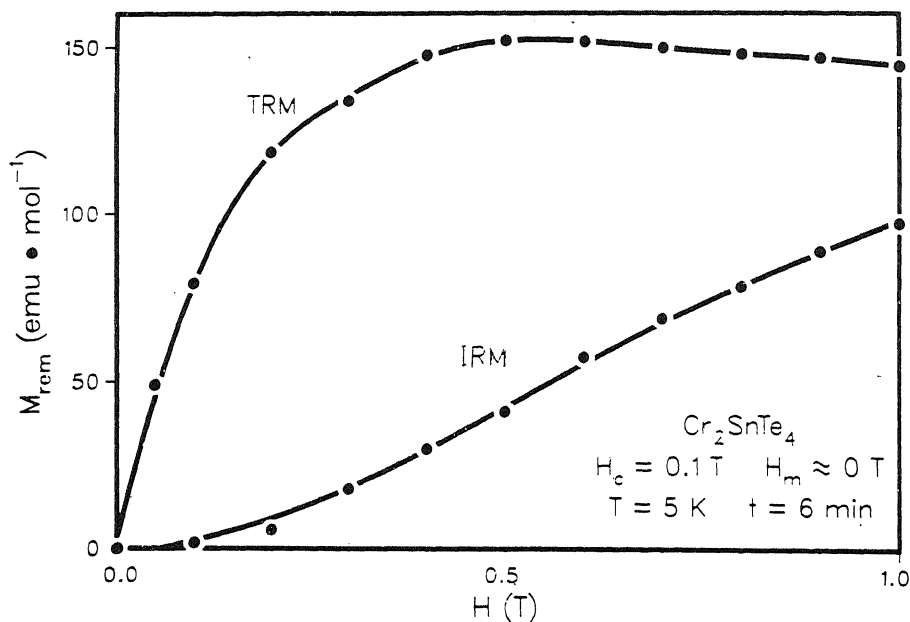


Figure 3. A plot of the IRM and TRM as a function of magnetic field for Cr_2SnTe_4 .

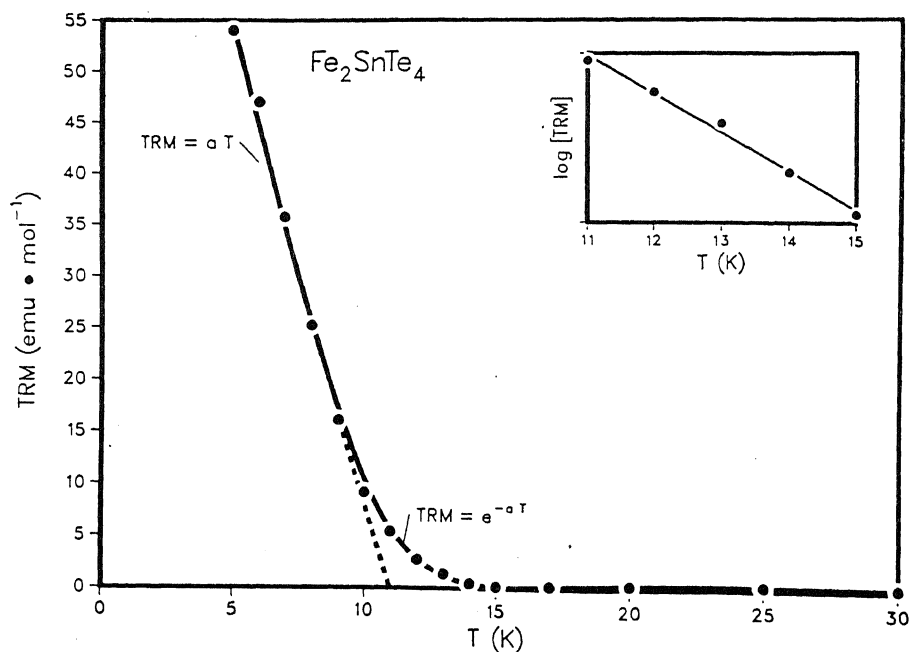


Figure 4. Plots of the TRM of Fe_2SnTe_4 plotted as a function of the temperature. Extrapolation of the TRM to zero is used to obtain the spin glass freezing temperature.

fluctuation and finally results in the freezing of the spins in their random positions. Bond disorder, topological disorder, or a combination of the two phenomena are also causes of frustration in amorphous materials. The random variance of the

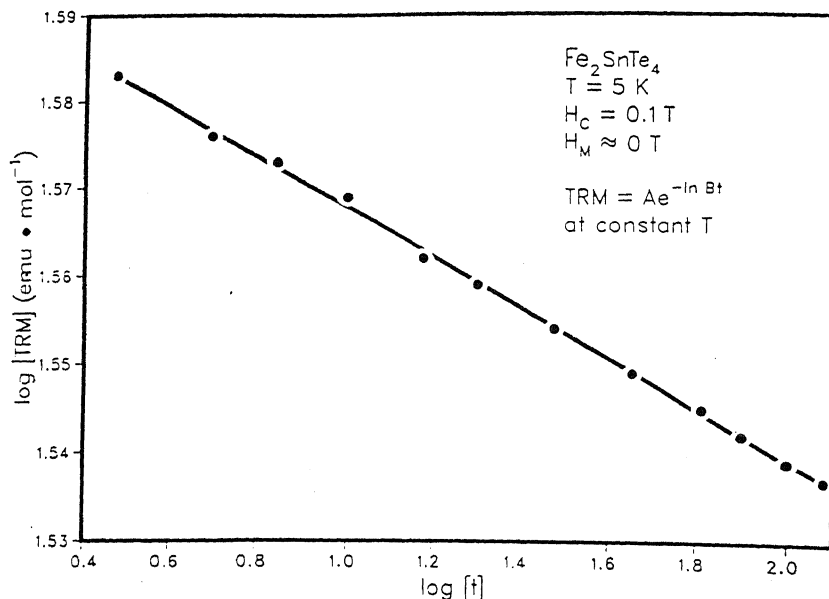


Figure 5. A log/log plot of the TRM of Fe₂SnTe₄ as a function of the time.

interactions in the three dimensional solid produces the frustration necessary for the spin glass "phase" often occurs in amorphous materials. However, the frustration of exchange interaction necessary for the spin glass state may also occur as the result of impurity centers in a crystal lattice.

The source of the frustration in these materials is likely due to a combination of bond disorder and topological disorder. The solid material has been reported to be a glassy metallic material that exhibits very little crystalline order. The material is also thermodynamically unstable with respect to the formation of the metal tellurides and the tin tellurides. For example, Fe₂SnTe₄ exhibits a powder pattern consistent with poor crystalline order. After heating this material for 24 hours at 600°C, the powder pattern exhibits peaks which may be indexed as FeTe_x and SnTe (Haushalter *et al* 1984a). The freshly prepared material exhibits spin glass behavior, as shown in figure 2, while the heat treated material exhibits an antiferromagnetic transition with a $T_N \sim 90 \text{ K}$, as shown in figure 6.

Several forms of iron tellurium alloys (FeTe_x) have been reported and these alloys exhibit a variety of magnetic properties (Hullinger 1968). For example, an alloy of stoichiometry FeTe_{1.1} exhibits normal Curie-Weiss behavior (Suchet and Serre 1965). Another alloy of stoichiometry FeTe_{0.95} exhibits antiferromagnetism with $T_N = 63 \text{ K}$ (Tsubokawa and Chiba 1959; Naya *et al* 1960). Some alloys of iron and tellurium with integral stoichiometric coefficients include FeTe which is an antiferromagnetic material with $T_N = 70 \text{ K}$ (Anon 1963), FeTe₂ which is also antiferromagnetic with $T_N = 83 \text{ K}$ (Llewellyn and Smith 1959), and Fe₉Te₈ which has a transition temperature $T_c = 63 \text{ K}$ and exhibits ferromagnetism above this temperature and ferrimagnetism below this temperature (Gronvold *et al* 1954). It is likely that we have prepared a phase that is related to the FeTe₂ phase, but with slightly different stoichiometry that permits increase in the Neel temperature to approximately 90 K.

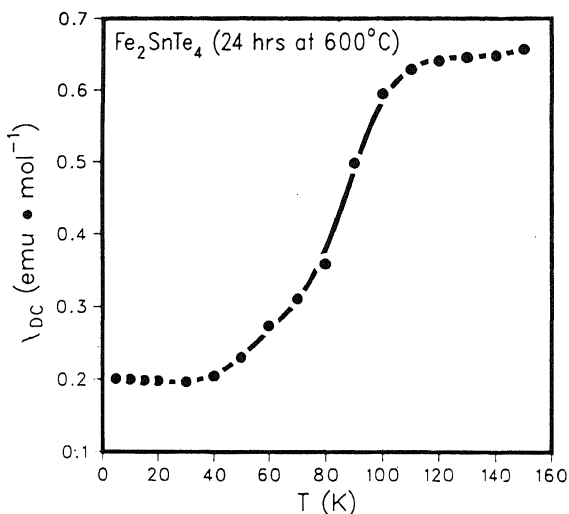


Figure 6. The magnetic susceptibility of a sample of Fe_2SnTe_4 after it was heat treated for 24 hours at 600 K. The freshly prepared material is amorphous, while the heat treated material behaves as a mixture of FeTe_x and SnTe , where the antiferro-magnetism is attributed to FeTe_x .

It is possible that the spin glass interactions in Fe_2SnTe_4 are the result of a frustration of the FeTe interactions. However, it is generally believed that the frustration necessary for a spin glass phase must result in an order of magnitude reduction in the ordering temperature (Moorjani and Corey 1985).

4. Conclusion

The materials of the formula M_2SnTe_4 are amorphous metallic alloys that exhibit a wide range of conductivities. These materials exhibit magnetic remanence and time dependence consistent with the spin glass state. The heated Fe_2SnTe_4 exhibits an antiferromagnetic transition at $T_N \sim 90$ K consistent with FeTe_x and SnTe decomposition products. The metallic character as measured by the conductivity shows a dependence on the reduction potential of the transition metal ion in solution. The properties of other magnetic systems prepared from K_4SnTe_4 will probably also provide systems that exhibit interesting magnetic behavior.

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Magnetochemistry of copper(II)

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Abstract. A selective review of some recent studies of the magnetic properties of compounds containing the spin $S = \frac{1}{2}$ copper(II) ion is presented. The emphasis lies with those compounds in which indirect exchange interactions are important. There is much variety, for there are dimers and clusters with either antiferromagnetic or ferromagnetic interactions, both uniform and alternating linear chains, two-dimensional or planar systems, and finally, some substances which exhibit predominantly three-dimensional interactions. In addition, recent *ab initio* and model calculations of indirect (super-) exchange interactions, responsible for the observed magnetic behavior, are discussed.

Keywords. Magnetochemistry; copper(II); antiferromagnetism; magnetic linear chains; planar magnets; superexchange.

1. Introduction

The paramagnetic properties of monomeric compounds of copper(II) are straightforward. This is due in large part to the fact that copper has but one unpaired electron irrespective of the local geometry and therefore always has spin $S = \frac{1}{2}$. The ground state in an octahedral complex is 2E_g ; the orbital degeneracy of the ground state is usually resolved by the Jahn-Teller effect. The g -values are often anisotropic, but are always of the order of 2.1 to 2.2; the effective magnetic moments are in the range $1.75\text{--}2.20 \mu_B$, where μ_B is the Bohr magneton. The moments are independent of temperature in the absence of cooperative effects. The epr spectra of more copper compounds than those of any other metal ion have been reported. Spin-orbit coupling is strong with copper, which is the source of the increase in the g -values above 2, yet the result of this effect is not nearly as dramatic as that with several other iron series ions. These properties stand in striking contrast to those of nickel(II), for example, whose planar compounds are diamagnetic and whose octahedral compounds are affected, at low temperatures, by zero-field splitting effects (Carlin and van Duyneveldt 1977; McGarvey 1966; O'Connor 1982; Bencini and Gatteschi 1982; Carlin 1986). Similarly, octahedral cobalt generally has g -values which are quite anisotropic, while the magnetochemistry of tetrahedral cobalt(II) is determined by the zero-field splitting of the 4A_2 state (Carlin 1985).

Perhaps the most notable feature of copper(II) chemistry and physics is the fact that this ion, with a doubly-degenerate electronic ground state, is susceptible to the Jahn-Teller effect. The coordination sphere is therefore generally distorted. In

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some cases, the coordination sphere is close to octahedral at room temperature and the distortion becomes important only as the temperature is lowered. This is often accompanied by a structural or lattice dynamical phase transition (Reiner and Friebe 1979).

Although many copper compounds exhibit such structural distortions, they nevertheless display relatively little magnetic anisotropy. In general, such anisotropy is due only to g -value anisotropy, which is typically about 5 or 10%. This leads copper, then, to be second only to manganese(II) in providing magnetically ordered compounds with only weak anisotropy (de Jongh and Miedema 1974). Such systems are found to follow what is called the Heisenberg magnetic model which is defined below.

Another feature of copper magnetochemistry is the high tendency the ion exhibits for ferromagnetic interactions. The series of compounds $A_2CuX_4 \cdot 2H_2O$ where A is an alkali metal ion or ammonium ion, and X is chloride or bromide, is one of the best-known series of ferromagnetic insulators (de Jongh and Miedema 1974). Ferromagnetic interactions predominate in such diverse materials as $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ (Algra *et al* 1977), $CuCl_2 \cdot DMSO$ (Swank *et al* 1979), and $(C_2H_5NH_3)_2CuCl_4$ (Steijger *et al* 1984).

Copper also has a tendency to form compounds in which there are two or more metal ions near one another. These polynuclear compounds often exhibit strong magnetic interactions between the copper ions, and the study of these has contributed greatly to our understanding of such magnetic exchange interactions. Furthermore, another important feature of the structural chemistry of copper is that compounds of different lattice dimensionalities are so readily available. The different behaviors, depending on this dimensionality, is one of the major themes of this article. This brief paper will review some of the recent theoretical and experimental work that is of interest in this area of magnetochemistry. The compounds discussed here are recently studied examples which are chosen to illustrate the varied physical phenomena.

Paramagnetic behavior is described by the Curie law, which is the magnetic analog of the ideal gas law. The magnetic susceptibility χ , which is a measure of the response of a material to an applied magnetic field, varies inversely with temperature according to the Curie law. This may be written as $\chi = C/T$, where C is called the Curie constant; in the common case of spin-only magnetism $C = Ng^2\mu_B^2S(S+1)/3k_B$, where N is Avogadro's number, S is the spin quantum number and k_B is the Boltzmann constant. Deviations from the Curie law are found as the temperature is decreased sufficiently for the magnetic ions to begin to interact with one another. This is described in a high-temperature approximation by the Curie-Weiss law, $\chi = C/(T-\theta)$ where the non-zero θ indicates that such interactions are present. This is a molecular field approximation; as we shall see more detailed models at the molecular level are available.

2. Dimers and clusters

The properties of hydrated copper acetate, $[Cu(OAc)_2(H_2O)]_2$, are well-known (O'Connor 1982; Carlin 1986) and illustrate many of the important concepts about magnetic interactions in copper compounds. The basic ideas concerning this

substance were worked out by Bleaney and Bowers (1952), and the model that they developed now goes by their names. The facts are that the susceptibility of copper acetate increases as the temperature is decreased from room temperature, goes through a maximum at about 255 K, and then decreases towards zero as the temperature is lowered further. This can be explained if $[\text{Cu}(\text{OAc})_2(\text{H}_2\text{O})]_2$ is actually a dimer and the metal ions are close enough together to interact with one another via the superexchange path provided by the bridging acetate ions. This exchange interaction between the two spin- $1/2$ ions results in a ground state with total spin $S = 0$ and an excited state with total spin $S = 1$. The interaction operator used to describe formally this type of interaction is the Heisenberg-Dirac-Van Vleck hamiltonian

$$H = -2JS_1 \cdot S_2 \quad (1)$$

in which S_1 and S_2 are the spin operators of the interacting ions and J is called the exchange constant. The energy separation $E(S = 1) - E(S = 0)$ is $-2J/k_B$, in energy units, and corresponds in $[\text{Cu}(\text{OAc})_2 \cdot (\text{H}_2\text{O})]_2$ to some 429 K. The negative value of the exchange constant indicates that the spin-singlet is the lower state (antiferromagnetic exchange coupling). If the exchange constant J has a positive sign, $S = 1$ level is lower, and this situation is called ferromagnetic exchange interaction. The susceptibility which arises from (1) is found as

$$\chi = \frac{2Ng^2\mu_B^2}{3k_B T} \cdot \frac{1}{1 + \frac{1}{2} \exp(-2J/k_B T)} \quad (2)$$

This relationship fits the experimental data excellently.

After the success of this analysis by Bleaney and Bowers, dozens, if not hundreds, of other copper dimers have been found which are well-described by (2). The vast majority have been shown to exhibit a negative exchange constant. A number of examples and literature references are provided by O'Connor (1982) and Carlin (1986).

The question arises then whether compounds can be found with a positive exchange constant, that is, with ferromagnetic intrapair interaction. The problem, as sample calculations with the Bleaney-Bowers equation quickly show, is that the susceptibility curve is then featureless and simply rises rapidly in Curie-Weiss fashion with decreasing temperature. Very accurate data and careful data analysis are required in order to prove that one has a half-mol of $S = 1$ dimers rather than a mol of $S = 1/2$ ions (Carlin 1986). Two compounds which were thought to have $S = 1$ ground states are $[\text{Cu}(\text{S}_2\text{CNET}_2)_2]$ and $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2(\text{NO}_3)_2]$. Both materials contain dimers in the crystal structure, but a comparison with the susceptibility of that of simpler salts, such as the Tutton salts, showed indeed that neither such compound exhibited strong pairwise ferromagnetic interactions (van Duijneveldt *et al* 1976; van Santen *et al* 1980; Carlin *et al* 1983).

In the case of $[\text{Cu}(\text{S}_2\text{CNET}_2)_2]$, the data suggest the existence of an intra-pair ferromagnetic interaction of 0.9 K, and a weak antiferromagnetic interaction of -0.007 K between the pairs. This is in contrast to the pairwise ferromagnetic interaction of 34.5 K reported earlier (McGregor *et al* 1973a,b). Similarly, in the case of $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2(\text{NO}_3)_2]$, the Curie-Weiss law was found to be obeyed at temperatures above 2 K and the data could be analysed in terms of non-interacting $S = 1/2$ copper ions (Carlin *et al* 1983). Any exchange interaction begins to manifest

itself only at temperatures of about 1.2 K. These data cannot be analysed in terms of the previously-reported ferromagnetic intra-pair interaction of about 14 K (McGregor *et al* 1973a,b).

A weak (0.22 K) ferromagnetic interaction has been found (Benelli *et al* 1985a) between the pairs of metal ions in *bis*-[(adenosine 5'-triphosphato) (2,2'-bipyridine) copper(II)] tetrahydrate. The metal atoms are held together by two O-P-O bridges from the α -phosphates of two ATP moieties. A determined effort to synthesize a variety of ferromagnetically ordered dimers has been carried out by Kahn and co-workers (Kahn *et al* 1983; Kahn 1985a,b).

Numerous efforts are still in progress to prepare and characterize copper dimers with spin $S = 1$ ground states. A curious situation arises when azide, N_3^- , is the bridging ligand, for it can bind in two ways (Kahn *et al* 1983; Sikorav *et al* 1984; Kahn 1985a,b). When the binuclear unit is of the form (chart 1)

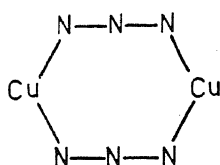


Chart 1

antiferromagnetic interaction is found. However, a compound with the different kind of binding (chart 2),

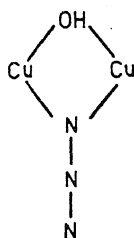


Chart 2.

has been suggested to exhibit a strong, intradimer ferromagnetic interaction. Cairns and Busch (1986) have recently reviewed ferromagnetic interactions in polynuclear complexes.

The range of possibilities offered by inorganic chemistry is emphasized by the recent studies on several bimetallic compounds of another kind (Bencini *et al* 1985; Bencini *et al* 1986; Vaziri and Carlin 1986). The lanthanides form few covalent bonds and there are few lanthanide compounds in which superexchange interactions are important. The unusual bimetallic materials contain a central gadolinium ion coordinated to two tetradentate Schiff bases of copper. The synthesis of such materials is straightforward, and the interesting point was the demonstration of the fact that the Gd-Cu exchange interaction is as large as 7 cm^{-1} (10 K) in strength and ferromagnetic in sign.

3. Magnetic linear chains

The magnetochemistry of copper(II) is an active field of research, with much of the attention centered on linear chain systems. By this, we mean substances whose magnetic interactions occur primarily in one dimension. These systems display extensive short-range order in the paramagnetic region. Before describing some of these materials, it will be useful to summarize several of the results due to Bonner and Fisher (1964).

The calculations of Bonner and Fisher are used frequently. Their model is the Heisenberg or isotropic antiferromagnetic linear chain; the Hamiltonian, a generalization of (1) is

$$H = -2J \sum_{i < j} \mathbf{S}_i \cdot \mathbf{S}_j \quad (3)$$

where the summation extends over all nearest-neighbor ions i and j in the chain. The authors calculated the behavior of both the zero-field susceptibility and the magnetic specific heat. A broad maximum is found in both; the susceptibility (in reduced units) is displayed in figure 1, over the range of validity of the calculation. Bonner and Fisher find that

$$k_B T_{\max} / |J| \approx 1.282, \quad (4)$$

and

$$\chi_{\max} |J| / N g^2 \mu_B^2 \approx 0.07346, \quad (5)$$

for the pure Heisenberg (isotropic) model, where $\chi_{\max}$ is the maximum value of the susceptibility, at temperature $T_{\max}$.

Copper forms many-chained compounds, some of them antiferromagnetic such as Cs_2CuCl_4 , and some of them ferromagnetic, as in $[(\text{CH}_3)_3\text{NH}]\text{CuCl}_3 \cdot 2\text{H}_2\text{O}$ (Losee *et al* 1972). Ferromagnetic linear-chain systems have recently been reviewed (Willett *et al* 1983).

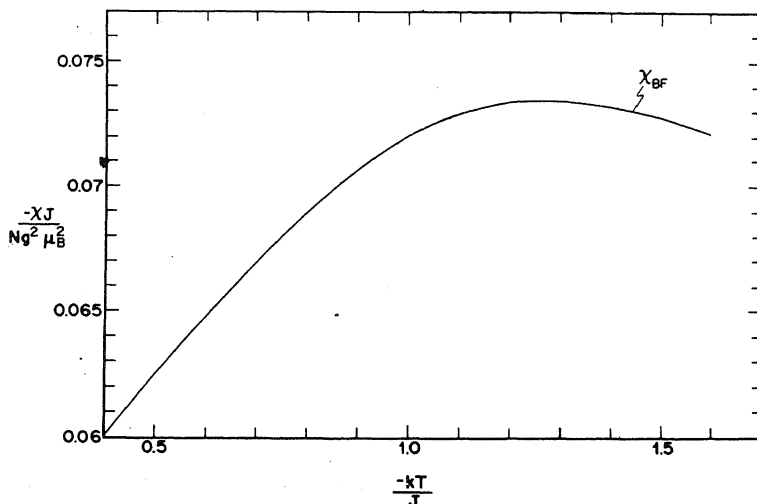


Figure 1. The calculated Bonner-Fisher susceptibility behavior, in reduced units.

The first example of a ferromagnetic spin $S = \frac{1}{2}$, Heisenberg linear chain was provided by $[(\text{CH}_3)_3\text{NH}]\text{CuCl}_3 \cdot 2\text{H}_2\text{O}$ (Algra *et al* 1977). The material contains planar $\text{CuCl}_2(\text{H}_2\text{O})_2$ ions which stack as an asymmetrical bibridged linear chain (Losee *et al* 1972). The water molecules lie above and below the plane defined by the $(\text{CuCl}_2)_n$ repeating units. Adjacent chains are hydrogen-bonded into sheets by an uncoordinated chloride ion, and then these sheets are separated by the bulky trimethylammonium ions.

The specific heat, figure 2, displays a broad maximum, characteristic of a system with extensive short-range order, and then a sharp peak at $T_c = 0.165$ K. This is the temperature of a phase transition from short-range order to long-range order. Only 28% of the magnetic entropy change occurs below T_c . The data cannot be analyzed simply in terms of a one-dimensional system; curve a) in the figure represents the specific heat of a ferromagnetic linear chain and does not fit the data below 1 K. The two-dimensional Heisenberg prediction, curve b), does not fit either. The observed values do lie between the two curves, however, indicating substantial interchain coupling. A 10% Ising-like anisotropy, curve c), causes the specific heat to rise again at lower temperatures. The data furthermore show the effects of lattice-dimensionality crossover: for $T > 1$ K, one-dimensional behavior is observed; two-dimensional behavior is found between 0.2 and 1 K. Finally, three-dimensional ordering behavior is seen below 0.2 K. The reanalysis of the susceptibility data (Algra *et al* 1977) is consistent with this analysis.

There are several linear chain systems which do not contain ligands bridging the metal ions in the usual fashion. One of these is CTN, $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$, which contains discrete, planar $[\text{Cu}(\text{NH}_3)_4]^{2+}$ units (Bhatia *et al* 1977) and another is Cs_2CuCl_4 (Carlin *et al* 1985). In the case of CTN, susceptibility maxima are found near 5 K, figure 3. Note the lack of anisotropy (except for that due to the different g -values) among the three data sets. The specific heat yields a maximum in the same temperature region, and then a small anomaly, due to long range ordering, which occurs at $T_c = 0.15$ K. Both sets of data may be fit by the model of Bonner and Fisher, and yield an antiferromagnetic exchange constant of $J/k_B = -3.9$ K. The values of T_c and J/k_B are compared in table 1 with those reported for several other copper chain compounds. One sees that $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$ is one of the

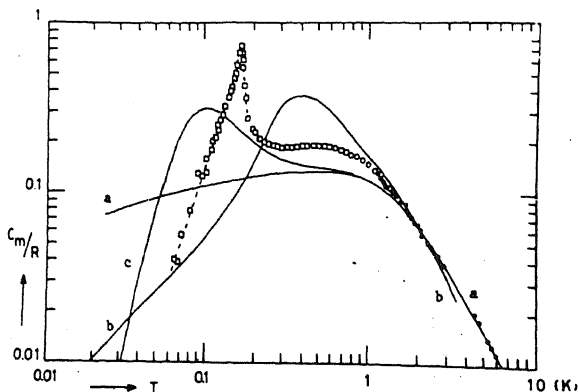


Figure 2. The magnetic specific heat of $[(\text{CH}_3)_3\text{NH}]\text{CuCl}_3 \cdot 2\text{H}_2\text{O}$ vs temperature, on a double logarithmic scale. The several curves are described in the text. From Algra *et al* (1977).

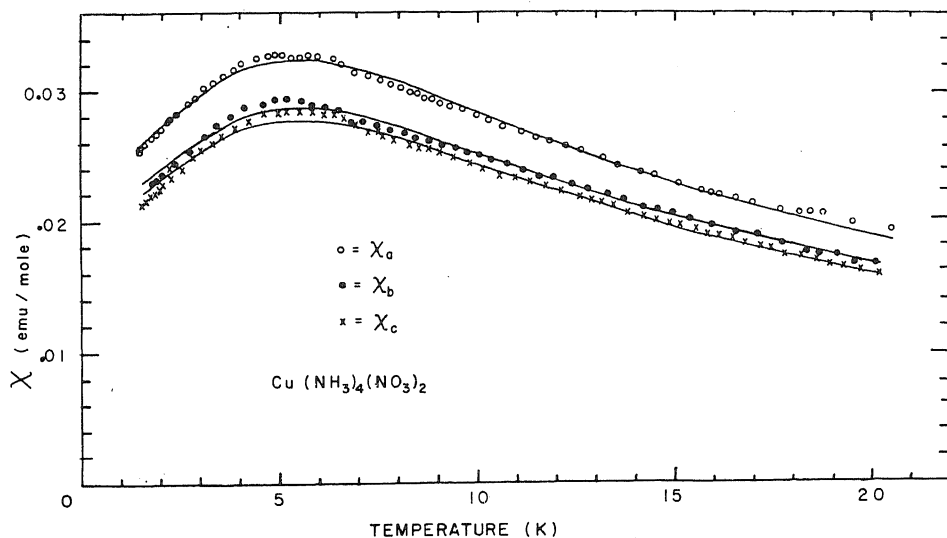


Figure 3. The three orthogonal susceptibilities of $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$, along with the best fits to the theory of Bonner and Fisher. From Bhatia *et al* (1977).

Table 1. Exchange parameters for some linear chain magnets.*

	$T_c(\text{K})$	$-J/k_B(\text{K})$	$k_B T_c/ J $
$\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$	0.43	3.15	0.137
$\text{CuCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$	1.13	13.4	0.084
$[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$	0.15	3.9	0.038
$[\text{Cu}(\text{pyrazine})(\text{NO}_3)_2]$	<0.05	5.20	<0.01
$[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$	0.142	1.02	0.193
TMMC	0.85	6.5	0.130

* All compounds are spin $S = \frac{1}{2}$ except for TMMC, which has $S = \frac{5}{2}$. Data are from Bhatia *et al* (1977) and Mennenga *et al* (1984).

more ideal one-dimensional antiferromagnets with spin value $S = \frac{1}{2}$. To compare with examples of other S , for example with the well-known TMMC, $[(\text{CH}_3)_4\text{MnCl}_3]$, we look at the quantity $t_c \equiv k_B T_c/|J|S(S+1)$, finding $t_c = 0.026$ for $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$ and $t_c = 0.015$ for TMMC ($S = \frac{5}{2}$). Thus the copper compound is only slightly inferior in approximating the ideal one-dimensional structure.

There has recently been a study (Carlin *et al* 1985) of Cs_2CuCl_4 , in which antiferromagnetic interactions occur over a relatively long superexchange path. The crystal structure is built up by the packing of discrete CuCl_4^{2-} anions and cesium ions; the anion is distorted, in that coordination around the metal is intermediate between square planar and tetrahedral. The compound is isomorphous with Cs_2CoCl_4 , a substance whose magnetic properties have been extensively investigated (McElearney *et al* 1977; Algra *et al* 1976; Duxbury *et al* 1981). Linear chain antiferromagnetic interactions have been found to predominate in Cs_2CoCl_4 , and they also dominate the magnetic ordering behavior of Cs_2CuCl_4 . An extensive

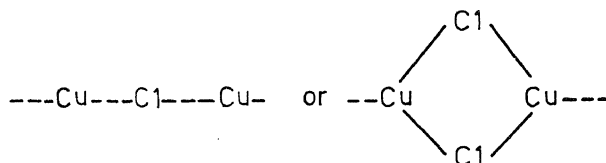
discussion of the exchange paths in Cs_2CoCl_4 and a rationalization of the linear chain character has been presented (McElearney *et al* 1977). The copper analog is found to behave somewhat similarly. The low-temperature susceptibility data on polycrystalline samples exhibit the broad maximum diagnostic of lower-dimensional antiferromagnetism.

The data above 10 K may be fit by the Curie-Weiss law for spin $S = \frac{1}{2}$, with $\langle g \rangle = 2.20$ and $\theta = -5$ K. The data then go through a broad maximum, with $\chi_{\text{max}} \approx 0.0665$ emu/mol at $T_{\text{max}} \approx 2.6\text{--}2.7$ K. The data were fitted to the calculations of Bonner and Fisher and gave a good fit with but one parameter, $-J/k_B = 2$ K.

The straightforward Bonner-Fisher procedure for the analysis of these data was also modified in terms of a molecular-field correction to this theory (McElearney *et al* 1973). That is,

$$\chi' = \frac{\chi_{\text{BF}}}{1 - (2zJ'/Ng^2\mu_B^2)\chi_{\text{BF}}} \quad (6)$$

Where χ_{BF} is the Bonner-Fisher calculation and χ' is the measured susceptibility. An adequate fit could be obtained with $J/k_B = -2.0$ K, and a molecular field correction of $zJ'/k_B = -0.10$ K. The molecular field correction is barely statistically significant. One of the major questions that remains in magnetochemistry research is the discovery of the empirical factors which determine whether the magnetic interactions will be antiferromagnetic or ferromagnetic in sign. The theoretical treatments of copper systems usually deal with metal ions which are μ -bridged by ligands, such as in a



moiety. The apparent interaction in Cs_2CuCl_4 is of the form Cu--Cl---Cl--Cu , of which there seem to be no previous examples in linear chain systems. There are however some two-dimensional systems with this configuration; they will be discussed below. The exchange interaction is remarkably strong for this lengthy superexchange path, as it also is for the two-dimensional systems.

There is an extensive series of compounds formed between the divalent iron series ions and pyridine N-oxide. A comprehensive review is available elsewhere (Carlin and de Jongh 1986). At room temperature all the compounds, including both $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ and $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$, are rhombohedral with one molecule in the unit cell. The coordination spheres are strictly octahedral but the magnetic behavior of the $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6]\text{X}_2$ compounds is controlled, at low temperatures, by the cooperative Jahn-Teller effect. The ligand $\text{C}_5\text{H}_5\text{NO}$ is pyridine N-oxide, and X is either perchlorate, fluoborate or nitrate.

The magnetic specific heat of $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$, shown in figure 4, is found to be excellently described by the Bonner-Fisher prediction for a $S = \frac{1}{2}$

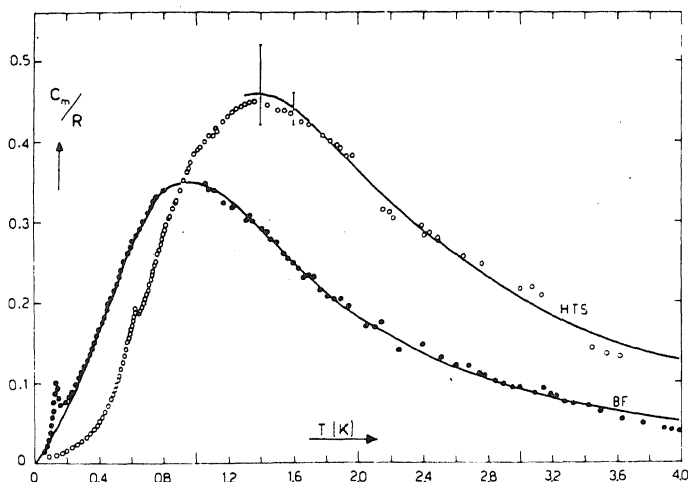


Figure 4. The magnetic specific heats for $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ and $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$ (● and ○, respectively). Curve B-F is the Bonner-Fisher (1964) prediction for a linear chain antiferromagnet with $J/k_B = -1.02$ K; curve H.T.S. is the prediction from the high-temperature series for the quadratic-layer antiferromagnet with $J/k_B = -1.10$ K. From Algra *et al* (1978a,b).

antiferromagnetic Heisenberg chain (Algra *et al* 1978a,b). The fit yields the intrachain exchange constant $J/k_B = -1.02$ K. Below $T \approx 0.3$ K deviations from the chain prediction are seen, which are ascribed to the weaker interchain interactions, leading to the onset of long-range order at $T_c = 0.142$ K. Below T_c , the experimental specific heat is found to be well represented by the sum of a T^3 dependence and the T^{-2} dependence arising from the hyperfine interactions. As regards the T^3 term, such a steep fall of the specific heat below T_c is usually observed in quasilinear chain compounds (de Jongh and Miedema 1974). Measurements (Reinen and Krause 1979) of the epr spectrum of the material confirmed this analysis. The epr spectra of these systems have yielded a great deal of information regarding the Jahn-Teller phenomena.

The substances Cs_2CuCl_4 , $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$, $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ and $\text{K}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$ (Blöte 1979) all exhibit (quasi-) linear chain antiferromagnetism and the copper atom is found in a discrete (non-bridging) polyhedron. Indeed, of the four substances listed, the first contains distorted tetrahedra, the second, planar coordination units, and distorted octahedra are found with the last two. None of the crystal structures are related nor are any of the structural details, such as the superexchange paths. The crystal lattices of both the pyridine N-oxide and nitro complexes have high symmetry at room temperature, but both undergo cooperative Jahn-Teller distortions as they cool. The one constant feature exhibited by this varied group of copper compounds is the existence of antiferromagnetic linear chain interactions.

The systems described above may be considered as uniform linear chains, in that the exchange constant between each metal ion in the chain has the same value. The subject of alternating linear chains has recently (de Groot *et al* 1982) become of interest, where the system is described by the Hamiltonian

$$H = -2J \sum_i (S_i \cdot S_{i-1} + \alpha S_i \cdot S_{i+1}) \quad (7)$$

The parameter α has the limiting values of 1 for a uniform chain and zero for a dimer, and $0 < \alpha < 1$ for an alternating chain. Thus the value of the exchange interaction between two metal ions depends on their location in the chain. The susceptibility behavior for an alternating chain is found to lie between that of the two extremes.

An example of such a material is provided (Benelli *et al* 1985b) by the adduct between the hexafluoroacetylacetonate of copper and the nitroxide, 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-N-oxy. The compound is called $\text{Cu}(\text{hfac})_2\text{TEMPOL}$. A sketch of the repeating unit in the structure is shown in figure 5. There is a strong (19 K) ferromagnetic interaction between the copper ion and the nitroxide, evident in the data taken above 4.2 K, and the susceptibility rises rapidly as the temperature is lowered below 1 K. Then a broad maximum, characteristic of an antiferromagnetic linear chain, is found at about 80 mK, figure 6. These data have been analysed in terms of a spin $S = 1$ linear chain, with a weak ($2J/k_B = -78$ mK) antiferromagnetic interaction between the spin-1 units. That is, the alternating character is obtained by repeating strong ferromagnetic and weak antiferromagnetic interaction. Similar results were also obtained from magnetization data on $(4\text{-benzylpiperidinium})\text{CuCl}_3$ (de Groot *et al* 1982).

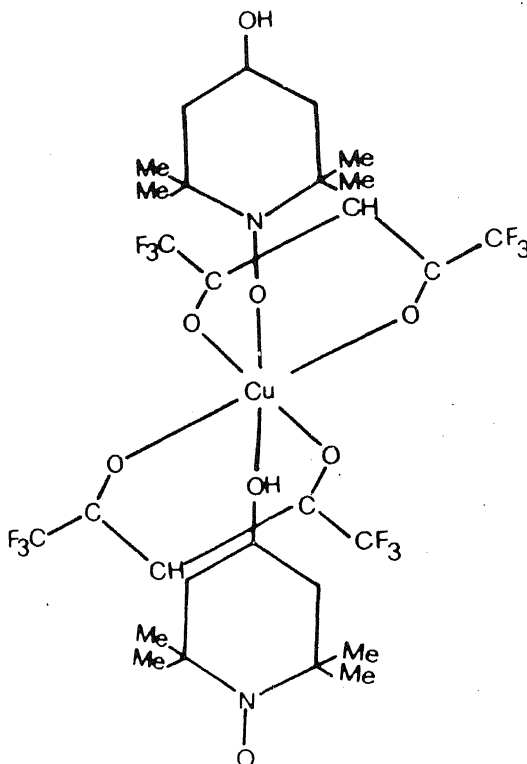


Figure 5. The repeating structural unit (schematic) of the $\text{Cu}(\text{hfac})_2\cdot\text{TEMPOL}$ chain. From Benelli *et al* (1985b).

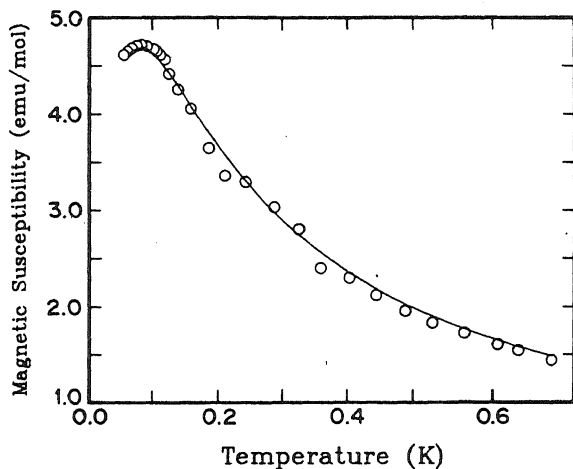


Figure 6. The low-temperature susceptibility data of $\text{Cu}(\text{hfac})_2 \cdot \text{TEMPOL}$, along with the fit described in the text. Note that the origin is off-set. From Benelli *et al* (1985b).

Another linear chain compound that has recently been studied (Mennenga *et al* 1984) is $[\text{Cu}(\text{pyrazine})(\text{NO}_3)_2]$, which contains copper ions bridged by the pyrazine rings. The aromatic ring appears to provide a substantial superexchange path. Broad maxima are evident near 5 K in both the susceptibility and the specific heat; the data may be fit by the Bonner-Fisher model with $J/k_B = -5.20$ K. Long range order is not observed above 50 mK, so that this material provides one of the best examples of a magnetic linear chain. The quantity t_c is less than 0.013 for $[\text{Cu}(\text{pyrazine})(\text{NO}_3)_2]$, which means that this compound is comparable to or even superior in approximating the ideal one-dimensional structure than the archetypal 1-d compound, TMMC.

Another feature of this material is that it exhibits evidence of random exchange effects. These are superimposed upon the behavior of the uniform Heisenberg linear chain and appear in the form of a strong increase in the susceptibility at low temperatures which is characteristic neither of the linear chain nor of a Curie-like impurity. The random exchange behavior is attributed to lattice defects, such as chain segments of finite size. Among these will be chain segments with an odd number of spins; in the present case, it was argued that the data could be explained if the chains consisted of about 200 copper spins on the average. The model is only applicable to the low temperature data.

The related series of compounds $[\text{CuCl}_2(\text{pyridine})_2]$, $[\text{CuCl}_2(3\text{-methylpyridine})_2]$, and $[\text{CuCl}_2(4\text{-methylpyridine})_2]$ have also been investigated (Wolthuis *et al* 1985). The room temperature structure in each case consists of chains of copper ions bridged by halide. The parent material, $[\text{CuCl}_2(\text{pyridine})_2]$, behaves as a uniform antiferromagnetic Bonner-Fisher chain with exchange constant $J/k_B = -13.4$ K, while the 4-picoline adduct behaves as an alternating chain with $J/k_B = -13.6$ K and an alternation parameter, α , of 0.6. The difference between the two compounds appears to arise from a freezing of methyl-group rotations in $[\text{CuCl}_2(4\text{-methylpyridine})_2]$ near 75 K which causes a dimerizing transition; this is evidenced by a sharp increase in dielectric permittivity at that

temperature. No such transition occurs with the 3-picoline adduct either, which also a uniform Heisenberg magnetic chain with $J/k_B = -12.4$ K.

The material $[\text{CuCl}_2(3\text{-methylpyridine})_2]$ was studied in an attempt to prepare samples with irregular methyl group orientation; indeed, by changing the rate of crystallization, the number of stacking faults was found to be variable. As with $[\text{Cu}(\text{pyrazine})(\text{NO}_3)_2]$, there is an extra, divergent contribution to the susceptibility at low temperatures that is superimposed on the uniform magnetic chain behavior. The contribution becomes more predominant the faster the rate of crystallization of the sample, but the effect has a much weaker temperature dependence in the present case than that found with the pyrazine compound.

4. Planar systems

There are many planar or two-dimensional magnets of copper(II). The best-known are probably the $(\text{RNH}_3)_2\text{CuCl}_4$ series, which consist of planar $(\text{CuCl}_4)_n$ sheets separated by the alkylammonium groups. Another example of planar antiferromagnetic magnets is provided by $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$, which is octahedral at room temperature. As it cools, it undergoes a cooperative Jahn-Teller transition, in this case to a two-dimensional magnetic system. It is fascinating that the fluoborate is isostructural with the perchlorate analog at room temperature, but that the perchlorate is a one-dimensional magnet at low temperatures. The packing of the distorted octahedra should be different in the two salts, since they must lead to a lack of overlapping unpaired electron densities in one and in two spatial directions for $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$ and $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$, respectively. The perchlorate undergoes an antiferrodistortive transition upon cooling below 60 K, while the fluoborate undergoes a ferrodistortive transition (Reinen and Krause 1979). Thus, the axes of elongation of the nearest neighbor ions in the distorted perchlorate are mutually orthogonal, while the axes of elongation are parallel in the low temperature phase of the fluoborate.

The magnetic specific heat of $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$ is also shown in figure 4 and is found to be in good agreement with predictions obtained for the quadratic $S = 1/2$ Heisenberg antiferromagnet (Navarro *et al* 1977). The fit of the high temperature series prediction to the experiment yields $J/k_B = -1.10$ K. The single crystal susceptibilities of $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$ have also been measured (A Lambrecq, R Burriel and R L Carlin, unpublished.) parallel and perpendicular to the three-fold axis as well as along one of the rhombohedral axes. The presence of three domains, confirmed by neutron diffraction measurements on this compound (Wood *et al* 1980), prevents the establishment of a macroscopic easy axis and thus a weighted average of $\chi_{\parallel}$ and $\chi_{\perp}$ is obtained. Only broad maxima are observed with little anisotropy.

In the above the magnetic contributions to the specific heat of $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ and $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$ have been compared. Although the magnetic behavior points to a lower-dimensional magnetic structure in both cases, very pronounced differences are found. Since the magnetic ordering phenomena occur at low temperatures, the magnetic specific heat is easily separated from the lattice contributions. The results for $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$ show very clearly that the specific heat of the quadratic Heisenberg antiferromagnet

net will have the form of a non-singular curve, with a broad maximum of height $c/R \approx 0.45$ at $k_B T/|J| \approx 1.3$.

A remarkable feature which emerges from the analyses is the fact that the *intrachain* exchange ($J/k_B = -1.02$ K) for $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ is so nearly equal to the *intralayer* exchange ($J/k_B = -1.10$ K) found for $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$. This implies that the Cu-O---O-Cu superexchange paths corresponding to these interactions should also be very nearly equivalent. This condition should in fact be very stringent in view of the extreme sensitivity of the interaction strengths to the interatomic distances. As mentioned earlier, we ascribe the lower-dimensional properties of both compounds to the occurrence of (static) Jahn-Teller distortion of the oxygen octahedra surrounding the Cu^{2+} ions.

There have been recently some experimental (Snively *et al* 1981; Rubenacker *et al* 1984, 1985) and theoretical (Block and Jansen 1982; Straatman *et al* 1984) studies of a new series of copper compounds, the alkanediammonium copper halides. A representative example is provided by the derivative of 1,2-ethanediamine, $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3]\text{CuCl}_4$. The structure consists of planar layers of CuCl_4^{2-} ions separated by organic chains which can be used to vary the interplanar separation. The copper ions in adjacent layers lie nearly directly above one another, so there can be a significant superexchange path between them via the two intervening halides. This exchange interaction along the linear Cu-Cl---Cl-Cu path has a significantly stronger dependence upon the Cu-Cu distance than expected normally, and is much larger than anticipated. Recall that a large exchange interaction for this path was also observed with Cs_2CuCl_4 . Block and co-workers have been able to reproduce this behavior theoretically.

5. Long range order

There are relatively few copper compounds which order three-dimensionally. The compounds described above which exhibit substantial short-range order generally undergo long-range order at some low temperature, but we refer here to materials which are primarily three-dimensional substances. The previously mentioned $\text{A}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ series of compounds falls in this class, as does $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (de Jongh and Miedema 1974). Another such substance is $[\text{Cu}(\text{en})_3]\text{SO}_4$, where the ligand is ethylenediamine, which orders at 109 mK (Carlin and Chirico 1981). This substance is trigonal at room temperature, but undergoes a cooperative Jahn-Teller distortion as it is cooled and is only triclinic in symmetry at 120 K and below. Nevertheless, the room-temperature unique (trigonal) axis is found to be the easy axis of antiferromagnetic alignment.

Another example of three-dimensional ordering is provided by $\text{CuL} \cdot \text{HCl}$, where $\text{H}_2\text{L} = 2,3$ -pyrazinedicarboxylic acid. The crystal structure of this material consists of polymeric chains which lie in a criss-cross fashion. This structure led to the suggestion (O'Connor *et al* 1982) that the material was a magnetic linear chain, with a small ferromagnetic interaction. Susceptibility measurements extended from 300 K down to 6 K, and a positive Weiss constant was observed. Measurements down to 1.1 K (Burriel *et al* 1985) could not, however, be fit by the calculations for a ferromagnetic Heisenberg linear chain, $S = 1/2$, nor could the fit be improved by introducing either spin or lattice anisotropy. An excellent fit of the data was

obtained on the other hand with the three-dimensional, (simple cubic), $S = \frac{1}{2}$, ferromagnetic Heisenberg model; the parameters are $\langle g \rangle = 2.18$ and $zJ/k_B = 2.610$ K.

This unexpected result suggested that measurements should be carried out to lower temperatures, and when this was done (Burriel *et al* 1985), the data shown in figure 7 were observed. Two sharp peaks, characteristic of long-range ferromagnetic ordering, were found, at 0.770 and 0.470 K. The behavior is typical of that of a powdered sample of a ferromagnetic material in which demagnetization effects become important (Carlin 1986). The existence of two peaks suggests that perhaps a spin-reorientation occurs at the temperature of the lower one. Perhaps dipolar interactions between copper ions in neighboring chains contribute to the ordering;

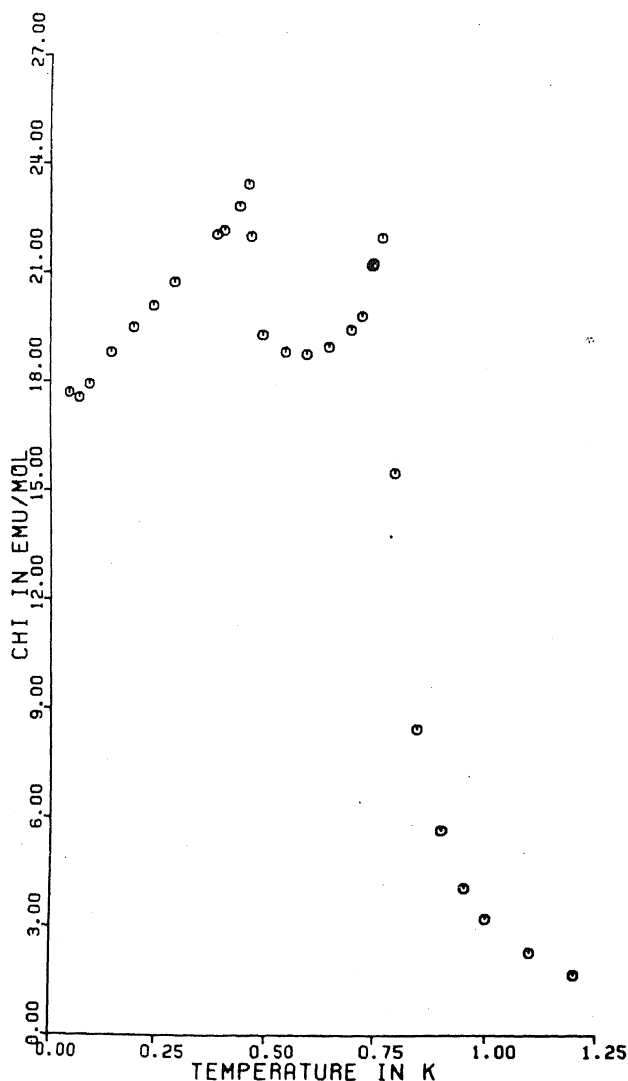


Figure 7. The susceptibility of CuL.HCl at low temperatures. From Burriel *et al* (1985).

whatever the cause, the data and the analysis require a three-dimensional magnetic interaction while only a one-dimensional superexchange path is apparent in the crystal structure. These results are a reminder that magnetic susceptibility measurements should be made in a temperature region where magnetic exchange makes a significant contribution to the measured quantity if inferences regarding the character of the magnetic exchange are to be made.

Another odd material is $[\text{Cu}(\text{NH}_3)_2(\text{CH}_3\text{COO})\text{Br}]$, which has a polymeric structure. The acetate ion bridges two copper ions such that the structure consists of zig-zag chains of coordination polyhedra running parallel to $[100]$. The Cu–O bond distances of the acetate which bridges the metal ions are the same (about 2 Å) but the Cu–O–C–O–Cu superexchange path is not a symmetric one, as in $[\text{Cu}(\text{OAc})_2(\text{H}_2\text{O})]_2$. From the predominant linear chain structure one would expect magnetic linear chain behavior, but this is in fact not found (Carlin *et al* 1986).

Specific heat measurements show that the material undergoes long-range order at 4.146 K, and there is no broad maximum, typical of lower-dimensional materials, noticeable in the data above T_c . Furthermore, the critical entropy, the amount of entropy acquired below T_c , is estimated as 42%, and is so large as to argue against substantial linear chain character. Nevertheless, the material appears not to obey the Curie-Weiss law at temperatures below 30 K, which is consistent with the presence of substantial short-range order. There is some indication that the material may best be viewed as an alternating linear chain, but the substance as yet is not well understood.

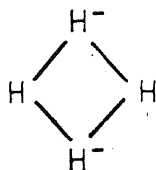
The materials discussed here should have interesting phase diagrams in an applied field (Carlin and van Duijneveldt 1980). These must be studied on large single crystals below the long-range ordering temperature, T_c . Since these substances order at such low temperatures, no such phase diagrams have yet been reported.

6. Theoretical aspects of superexchange

The accurate experimental results on the weak ferromagnetic and antiferromagnetic interactions, available on a variety of solids and molecular complexes, have stimulated a number of theoretical efforts to formulate a quantitative description of this phenomenon. Analysis on this subject, ranging from a crude semi-empirical level to large scale *ab initio* methods, can be found in the literature (de Loth *et al* 1981). It appears, however, that the weakness of the interactions (usually several hundred Kelvin or less) generally puts too excessive a demand on the accuracy of the first-principles calculations. Moreover, in evaluating final expressions obtained in *ab initio* treatments, empirical parameters such as ionization potentials and covalency parameters deduced from hyperfine splitting data are often used, thus rendering these methods semi-empirical (Wachters and Nieuwpoort 1972; Fuchikami 1970). Even present-day calculations have not eliminated the intrinsic problems (e.g., persistent basis-set deficiencies, superposition errors and slow convergence of electron-correlation contributions) arising in the milliHartree energy range and below. In this context we mention the recent calculations by de Loth *et al* (1981, 1985), Daudey *et al* (1985), and Astheimer (1986) in exchange-coupled copper(II)

dimers. The singlet-triplet splitting energy is obtained by a perturbative treatment of configuration interaction (up to and including 4th order), which is closely related to Anderson's (1963) formalism. Although fair agreement with the experimental data is claimed, it is of interest to observe the successive contributions in the perturbation expansion. As an example we have listed in table 2 the numerical values of the different contributions to the singlet-triplet splitting energy calculated by de Loth *et al* (1985) for the dimeric complex $\{\text{CuBr}[\text{OCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2]\}$. Apart from the lack of convergence in the expansion, it should be noted that the method itself is open for discussion: the first-order interaction term, the potential exchange, is always of ferromagnetic sign whereas the required antiferromagnetic contributions to the exchange constant only arise at second- and higher-order of perturbation which make the CI expansion rather poor (Noodleman 1981).

Instead of adopting such extended calculational schemes, one also defines *a priori* simple theoretical models, affording an accurate quantitative evaluation of the exchange constant, in which it is assumed that relevant quantum-mechanical characteristics for the interactions are retained. Such model approaches show the advantage of covering exchange coupling in a series of chemically and structurally related compounds, and have been proposed by, e.g., Hay *et al* (1975), Kahn and Briat (1976), Harcourt (1976) and Jansen and Block (1977). A discussion and numerical comparison of these methods is given by van Kalker *et al* (1979). Irrespective of their differences in the pre-suppositions of the relevant quantum-mechanical basis, the methods show, for example, the same qualitative behavior with respect to geometrical variation of the superexchange unit M-L-M. For values of the bridging angle around 90° , the angular dependence of the exchange constant is found to be large and a ferromagnetic coupling becomes quite possible in a small range of the angle. The same trend was obtained in a model analysis of the exchange coupling between two paramagnetic cations *doubly* bridged by two diamagnetic ligands (Bominaar and Block 1983). The model used was a four-center, six-electron description of the superexchange unit (symmetry D_{2h}) with 1s Slater-type orbitals corresponding to a



system. In this study it is also shown that the ligand potentials, often at best roughly accounted for in the various models, are essential in the evaluation of the exchange constant.

Recently, the exchange-channel model (Eremin and Rakitin 1978) has been compared numerically with the effective-electron model of Jansen and Block (1977) for the prediction of exchange constants in linear M-L-M units (for M = Sc to Cu; L = F, Cl and Br) (Bominaar and Block 1986). Although completely different in their basic assumptions, a striking mutual consistency in the results was found.

Table 2. Numerical values of the different contributions to the singlet-triplet energy (in cm^{-1}) according to de Loth *et al* (1985).

Potential exchange	710
Kinetic exchange	-972
Double spin polarization	46
Charge-transfer, ligand $\rightarrow$ copper	-292
Charge-transfer, copper $\rightarrow$ ligand	-24
Second order exchange + polarization	-134
Fourth order exchange + polarization	-430
Total	-1095
Experimental value	-817

Following previous effective-electron model calculations of exchange constants in superexchange units with one (de Jongh and Block 1975), two (van Kalker *et al* 1978), and even three (ter Maten and Jansen 1978) bridging ligands, the inter-layer antiferromagnetic interaction in the alkane-diammonium copper halides (cf. above) was studied (Block and Jansen 1982; Straatman *et al* 1984). In this model the number of electrons is drastically reduced to *one* per cation and *two* spin-paired electrons for each intervening anion. These electrons occupy "effective" orbitals of spherical symmetry with consistently determined extensions. The numerical results obtained for the exchange constants in the lengthy, linear $\text{Cu-X}\cdots\text{X-Cu}$ paths, with $\text{X} = \text{Cl}$ or Br , are found to agree with experiment, provided that the observed non-linearity in a few units was taken seriously. The latter effect of non-linearity in the two-halogen bridge on the calculated value of J is quite substantial.

7. Conclusions

Copper forms many compounds with important lower dimensional character; we include dimers and clusters in this phrase. One interesting fact is the existence of relatively few materials which order as three-dimensional materials; perhaps the reason for this is that the metal ions have to be well-separated and thus ordering of 3-D systems will be found at temperatures below 1 K. In any case, it seems to be worthwhile to search for more copper compounds which order three-dimensionally.

The field-dependent behavior of the compounds described would also be useful to explore; the observation of spin-flop would yield several interesting parameters.

As far as the theoretical calculation of exchange constants is concerned, the state of *ab initio* theory still implies an evident need of model calculations which describe satisfactorily the observed trends and systematics.

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Structural and electronic properties of six-coordinate Lewis-base adducts of iron(III) Schiff-base complexes. Crystal structure and magnetism of the high-spin complex [(imidazole)Fe(salen)(NCS)]–0.5 MeOH and of a related complex containing two dissimilar axial ligands

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Abstract. The structural and electronic properties of two high-spin iron(III) Schiff-base complexes [(imd)Fe(salen)(NCS)] (I) and [(imd)Fe(salen)(N₃)] (II) are described. Crystals of I as a hemimethanol solvate, (C₃H₄N₂)Fe(C₁₆H₁₄N₂O₂)(NCS).0.5 CH₃OH, crystallize in the triclinic space group *P*1̄ with unit cell dimensions *a* = 14.278(4), *b* = 16.932(4), *c* = 9.057(4) Å, α = 97.40(3), β = 92.07(3), γ = 85.32(2)° and *Z* = 4. The structure was refined by a block-matrix least-squares procedure to final *R* 0.050 and *R*_w 0.057 using 3127 unique reflections with *I* > 2.5 σ (*I*). Complex I is one of the few structurally characterized examples of six-coordinate Lewis-base adducts in which there are two different axial ligands. The in-plane Fe–N distances, 2.12 Å (av) are characteristic of *S* = 5/2 Fe^{III}. The Fe–N (imidazole) distance of 2.149(5) Å is similar to that in related high-spin imidazole-Fe^{III} complexes. Non-linear Fe–NCS bonding is observed (Fe–N–C = 159.0(5)°) as in related six-coordinate Fe^{III} porphyrin and methemoglobin isothiocyanate species. Mössbauer spectra of I and II between 295 and 4.2 K are symptomatic of *S* = 5/2 Fe^{III}. The nature of the asymmetry of the quadrupole doublet as a function of temperature points to zero field splitting of the ⁶A₁ ground state having a negative value of the axial ZFS parameter, *D*. These are new additions to the few known examples of negative *D* in Fe^{III}-tetradentate chelating systems, and contrast for instance with aquo-imidazole Fe^{III} salen adducts which we have recently shown to have positive *D* values. Spin-hamiltonian analyses of the 300–4.2 K χ_{Fe}/T data, assuming rhombic ligand field symmetry, yielded the following parameter sets; I: *g* = 1.98 ± 0.02, *D* = –2.4 ± 0.2 cm^{–1}, *E* = 0.6 ± 0.2 cm^{–1}. II: *g* = 2.00 ± 0.01, *D* = –1.4 ± 0.2 cm^{–1}, *E* = 0.4 ± 0.2 cm^{–1}. In the 77 K X-band ESR spectra of neat powdered samples of II: a line at *g* = 4.4 confirms the rhombic splitting, while the related spectrum for I shows a broad line at *g* ~ 2.1. This somewhat unusual line position probably arises through solid state exchange effects since a *g* 4.3 signal is observed for a frozen glass spectrum.

Keywords. Six-coordinate Lewis-base adducts; iron(III) Schiff-base complexes; (imidazole)Fe(salen)(NCS); high spin complex; magnetism; Mossbauer spectra.

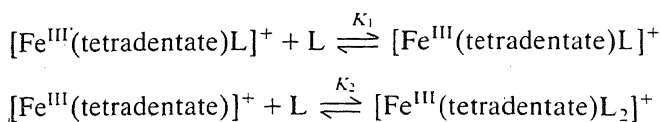
1. Introduction

Six-coordinate iron(III) complexes display a variety of electronic ground states, viz high-spin (*S* = 5/2), intermediate-spin (*S* = 3/2) or low-spin (*S* = 1/2) as well as spin-crossover behaviour (Mitra 1982). The precise nature of the ground state, which is often perturbed by other low lying states, is dependent on the bonding

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properties of the coordinated ligands. Often small changes in the coordinating groups, and/or in the nature of non-coordinating anions or molecules of solvation can cause dramatic differences in the observed magnetic properties. These features are observed in complexes of type $[\text{Fe}(\text{tetradentate})\text{L}_2]\text{X}$ formed by the reaction of a Lewis-base (L) such as imidazole (imd) or pyridine (py) with tetradentate porphyrin or Schiff-base iron(III) complexes (Collman *et al* 1978; Nishida *et al* 1975, 1977; Scheidt *et al* 1979, 1983a; Hill *et al* 1979; Scheidt and Reed 1980; Gregson 1981; Maeda *et al* 1982; Ohshio *et al* 1983; Kennedy 1984; Kennedy *et al* 1987).

Addition of a Lewis-base to these complexes is thought to proceed in two stages (La Mar and Walker 1972; Walker *et al* 1976; Satterlee *et al* 1976)



Formation and isolation of the *bis*-adduct is usually favoured in comparison to the mono-adduct and consequently many studies of the structural and magnetic properties of the *bis* adducts have been made. However, from the bioinorganic point of view, since many heme proteins contain only one bonded axial histidine residue, considerable interest has evolved recently in the synthesis and study of mono-imidazole adducts of these Fe^{III} chelates. Unfortunately the isolation of pure crystalline samples of such adducts has often proved difficult and this has therefore impeded progress in obtaining mono-base model compounds.

Recently, however, Scheidt and co-workers have reported structural studies of some porphyrin complexes of the type $[\text{Fe}(\text{por})(\text{py})\text{X}]$ ($\text{X} = \text{NCS}^-$, N_3^- , CN^- , $\text{por} = \text{TPP}^{2-}$, OEP^{2-}) (Scheidt *et al* 1982, 1983b; Adams *et al* 1979). Variations in the porphyrin and X ligands led to high-spin or high-spin $\rightleftharpoons$ low-spin crossover complexes being obtained. A recently isolated phase of $[\text{Fe}(\text{TPP})(\text{py})(\text{NCS})]$ contains both of these electronic forms (Geiger *et al* 1985). However, the presence of variable amounts of apparently solvated Lewis base molecules has made a rigorous study of the magnetic properties of these six-coordinate moieties difficult. Our own recent work on the related Schiff-base systems (Kennedy 1984; Kennedy *et al* 1984, 1985, 1987) has indicated that, with suitable care, the mixed ligand complexes could be isolated, without containing any extra Lewis-base molecules. In this paper we describe the crystal structure of one such compound, $[(\text{imd})\text{Fe}(\text{salen})(\text{NCS})]$, **I**, and relate the structural features to the electronic properties of the molecule. A detailed investigation of magnetic susceptibilities, ESR and Mössbauer spectra for this d^5 high-spin complex has yielded information on the zero-field splitting of the 6A_1 ground state. Similar data are discussed for the analogous azido complex, $[(\text{imd})\text{Fe}(\text{salen})(\text{N}_3)]$ (**II**). The crystal structure is not available for **II** but that of the related cobalt(III) complex $[(\text{py})\text{Co}(\text{acen})(\text{N}_3)]$ is known (Clearfield *et al* 1978).

2. Experimental section

2.1 Synthesis

$[\text{Fe}(\text{salen})(\text{NCS})]$ and $[\text{Fe}(\text{salen})(\text{N}_3)]$ were prepared as described by Gullotti *et al* (1977).

[(*imd*)Fe(salen)(NCS)] (I): 0.5 g of [Fe(salen)(NCS)] were suspended in 40 ml of absolute methanol and 0.5 g of imidazole added. The solution was then refluxed for 15 minutes during which time most of the solid dissolved. Any undissolved solid was then removed from the hot solution and, on cooling overnight, small black crystals were deposited. These were filtered, washed twice with ice-cold methanol, and then dried in air.

The same crystalline product could be obtained by refluxing Fe(salen)Cl and excess imidazole in methanol for 10 minutes, followed by addition of a 2 molar excess of sodium thiocyanate. IR spectrum: $\nu(\text{NCS})$ 2080 cm^{-1} .

[(*imd*)Fe(salen)(N₃)] (II): This compound was prepared from [Fe(salen)(N₃)] in an analogous manner to that described above. IR spectrum: $\nu(\text{N}_3)$ 2080 cm^{-1} .

Satisfactory analytical data were obtained for both complexes.

Crystals of [(*imd*)Fe(salen)(NCS)] suitable for the x-ray diffraction study were obtained by slow evaporation of a methanol solution. The crystal structure showed the presence of 0.5 mol of methanol of solvation.

2.2 Physical methods

Magnetic susceptibilities were measured in a field of 10 kG on an Oxford Instruments Faraday Balance (Mackey *et al* 1976). Samples were carefully checked for any anomalous field dependence at both 4.2 K and 300 K, but none was found to be present.

ESR and Mössbauer spectra were obtained as described elsewhere (Mitchell *et al* 1977). The isomer shifts are relative to iron metal at room temperature.

2.3 X-ray crystal structure determination of I

A black-prism was mounted on a glass fibre and coated with cyano-acrylate super glue. Lattice parameters at 295 K were determined by a least-squares procedure on the setting angles of 25 reflections measured with MoK α radiation (λ 0.71073 Å) on an Enraf-Nonius CAD4 diffractometer. Intensity data on this crystal were collected using an ω : ($n/3$) θ scan where n (= 2) was optimized by profile analysis of a number of representative reflections. No significant decomposition of the crystal occurred during the data collection. Correction was applied for Lorentz and polarization effects using the program SUSCAD (Guss 1979) and for absorption using the appropriate procedure in SHELX (Sheldrick 1976). Crystallographic data are summarized in table 1.

The structure was solved using the program MULTAN and refined by a block-matrix least-squares procedure in which the function $\sum \omega \Delta^2$ was minimized (Guss 1979). Anisotropic thermal parameters were introduced for all non-hydrogen atoms and a weighting scheme, $1.47/[\sigma^2(F) + 0.0021|F|^2]$, included. The refinement converged with final values for R and R_w 0.050 and 0.057, respectively. Hydrogen atoms were not included in the model and no correction was made for extinction. The analysis of variance showed no special features and the maximum residual electron density peak in the final difference map was 0.52 eÅ⁻³. The assignment of the 'ambiguous' N(5) and C(19) atoms of the imidazole group was confirmed by interchanging the atoms and refining the model. The result of this procedure was an increase in R and the presence of non-sensible thermal ellipsoids.

Table 1. Summary of the crystallographic data for (imd)Fe(salen)(NCS)·0.5 MeOH (I).

Formula	C _{20.5} H ₁₆ N ₅ O _{2.5} SFe
mol. wt.	460.3
crystal system	triclinic
space group	$P\bar{1}$ (C_1^1 , No. 2)
<i>a</i> , Å	14.278(4)
<i>b</i> , Å	16.932(4)
<i>c</i> , Å	9.057(4)
α , °	97.40(3)
β , °	92.07(3)
γ , °	85.32(2)
<i>U</i> , Å ³	2163.4
<i>d</i> _{calcd} (<i>d</i> _{obs}), Mg/m ³	1.41 (1.45)
crystal dimensions, mm ³	0.15 × 0.45 × 0.50
radiation	MoK α , (graphite monochromator)
absorption coefficient, μ , mm ⁻¹	0.785
transmission factors (max/min)	0.886, 0.734
temperature K	297
omega scan angle, °	(1.90 + 0.35 tan θ)
horizontal counter apertures, mm	(2.40 + 0.5 tan θ) ;
data collected	1.3 ≤ θ ≤ 21°, ($\pm$ h, $\pm$ k, l)
total reflections	4581
<i>R</i> _{merge}	0.023
unique data, <i>I</i> ≥ 2.5σ(<i>I</i>)	4376, 3126
<i>R</i> (<i>R</i> _w)	0.050 (0.057)
largest Δ/σ, eÅ ⁻³	0.52

Scattering factors for neutral Fe were from Ibers and Hamilton (1974), the terms having been corrected for $\Delta f'$ and $\Delta f''$ and those of the remaining atoms were those incorporated in the SHELX system. Final fractional coordinates are listed in table 2. The associated anisotropic thermal parameters are given in the Supplementary Material as are lists of observed and calculated structure factors and complete lists of bond lengths and bond angles.

3. Results and discussion

The products from the reaction of Fe(salen)X (X = SCN, N₃) with excess imidazole are the mixed ligand complexes [(imd)Fe(salen)(NCS)] (I) and [(imd)Fe(salen)(N₃)] (II). Even when extremely large excesses of the Lewis base were used there is no evidence to suggest that any *bis*-adducts are present in the polycrystalline products although, as shown below, such species can form in solution and are expected to be present in the reaction mixture (Kennedy *et al* 1985, 1987). The relative stability of the mixed ligand complex in the present case can be compared to the complicated equilibria found for the related iron(III) porphyrin complexes where the formation of the mono-imidazole adducts is favoured only for a very small ratio of imidazole to porphyrin with larger ratios yielding the corresponding *bis*-adduct (Scheidt *et al* 1982, 1983; Adams *et al* 1979).

Repeated attempts to isolate the *bis* adducts $[\text{Fe}(\text{salen})(\text{imd})_2]\text{X}$ ($\text{X} = \text{SCN}$ or N_3) were unsuccessful as were attempts to prepare the analogous chloride complex $[\text{Fe}(\text{salen})(\text{imd})_n]\text{Cl}$ ($n = 1$ or 2). Indeed with the chloride only the starting product or the μ -oxo dimer $[\text{Fe}(\text{salen})]_2\text{O}$ could be isolated from the reaction solutions. The *bis*-imidazole compounds can be crystallized when a large anion such as ClO_4^- , BF_4^- or PF_6^- is present. The structures and properties of these compounds are described elsewhere (Kennedy 1984; Kennedy *et al* 1987).

3.1 Crystal and molecular structure of I

The numbering scheme is shown in figure 1, which highlights the molecular structure of the complex. There are two crystallographically distinct molecules in the asymmetric unit; the numbering of the second molecule is the same as in figure 1 but with an asterisk on each atom. Individual bond lengths and angles in the two molecules are very similar with only minor differences noted (tables 3 and 4). The different molecules are seen in the crystal packing diagram shown in figure 2. Also

Table 2. Non hydrogen atom coordinates for $(\text{imd})\text{Fe}(\text{salen})(\text{NCS}) \cdot 0.5 \text{ MeOH}(\text{I})^{\text{a,b}}$.

Atom	x	y	z	Atom	x	y	z
Fe	55673(6)	76766(5)	2628(9)	C(13)	4870(5)	6000(4)	3878(8)
Fe(*)	03895(6)	72012(5)	31889(9)	C(14)	4303(5)	6284(5)	5062(9)
S(1)	3016(1)	6060(1)	-1264(2)	C(15)	3977(5)	7104(5)	5270(8)
S(1')	7627(1)	5890(1)	4045(2)	C(16)	4227(5)	7626(4)	4299(7)
O(1)	5278(3)	8633(2)	-667(4)	C(17)	4822(4)	7323(4)	3082(7)
O(2)	5058(3)	7854(2)	2205(4)	C(18)	7427(5)	7817(4)	2124(7)
O(1')	9756(3)	8066(3)	4459(4)	C(19)	7987(5)	8966(5)	1849(10)
O(2')	9859(3)	7319(2)	1283(4)	C(20)	7199(5)	8867(5)	945(9)
N(1)	4323(4)	7189(3)	-530(6)	C(1'')	8643(4)	6205(3)	3764(6)
N(2)	6166(3)	7152(3)	-1782(5)	C(2'')	9911(5)	8325(4)	5905(7)
N(3)	6082(3)	6528(3)	716(6)	C(3'')	9360(7)	8993(6)	6510(9)
N(4)	6862(3)	8141(3)	1126(5)	C(4'')	9473(8)	9287(6)	8023(11)
N(5)	8118(4)	8313(3)	2606(6)	C(5'')	10107(8)	8911(6)	8923(10)
N(1')	9358(4)	6433(3)	3559(6)	C(6'')	10657(6)	8234(5)	8342(8)
N(2')	11137(3)	6829(3)	5040(5)	C(7'')	10540(5)	7940(4)	6829(7)
N(3')	11252(3)	6231(3)	2213(6)	C(8'')	11120(5)	7197(4)	6365(7)
N(4')	11468(3)	7966(3)	2851(6)	C(9'')	11644(5)	6030(4)	4791(8)
N(5')	12531(4)	8521(4)	1686(7)	C(10'')	12017(5)	5927(5)	3183(8)
C(1)	3788(4)	6718(4)	-829(7)	C(11'')	11110(5)	5841(4)	892(7)
C(2)	5599(4)	8876(4)	-1898(7)	C(12'')	10386(5)	6093(4)	-156(7)
C(3)	5378(5)	9677(4)	-2113(7)	C(13'')	10328(6)	5583(5)	-1525(9)
C(4)	5682(6)	9954(5)	-3407(9)	C(14'')	9659(7)	5766(5)	-2599(8)
C(5)	6193(6)	9449(6)	-4459(9)	C(15'')	9051(5)	6449(5)	-2344(8)
C(6)	6396(6)	8671(6)	-4252(8)	C(16'')	9093(5)	6977(5)	-1038(8)
C(7)	6101(4)	8354(4)	-2964(7)	C(17'')	9789(4)	6792(4)	82(7)
C(8)	6314(5)	7509(4)	-2910(7)	C(18'')	12066(5)	7853(5)	1759(8)
C(9)	6346(6)	6274(4)	-1913(9)	C(19'')	12209(6)	9064(5)	2818(12)
C(10)	6728(5)	6074(4)	-387(8)	C(20'')	11559(6)	8732(5)	3521(11)
C(11)	5771(4)	6147(4)	1733(8)	O	6598(4)	889(3)	560(7)
C(12)	5136(4)	6521(4)	2877(7)	C	6967(7)	1096(7)	2031(13)

^a Fe coordinates $\times 10^5$; other atom coordinates $\times 10^4$

^b Atoms labelled with an asterisk refer to the second distinct molecule in the asymmetric unit. Atom C and O are for methanol.

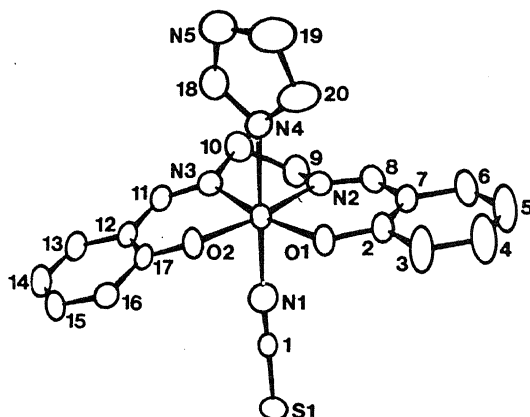


Figure 1. Molecular structure and numbering scheme for **I**. Atoms otherwise not indicated are carbon atoms.

evident are methanol molecules of solvation which are present in the ratio of one MeOH to two [(imd)Fe(salen)(NCS)]. Both of the molecules of **I** are involved in weak intermolecular hydrogen-bonding to the solvate molecule. The two closest intermolecular contacts in the structure occur between the oxygen atom of MeOH and O(1)^a of 2.736 Å and N(5')^b of 2.755 Å (where superscripts *a* and *b* refer to the symmetry operations 1 - *x*, 1 - *y*, - *z*, and 2 - *x*, 1 - *y*, - *z*, respectively). In this context it is noteworthy that the Fe-O(1) distance in each of the two molecules is not significantly different from the Fe-O(2) distance so that it is unlikely that the presence of the intermolecular contact described above influences the nature of the Fe atom environment.

Figure 1 shows that iron exists in a distorted octahedral environment defined by the O(1), O(2), N(3), N(2) donor atoms of salen in the basal plane, the N(1) atom of the end-on isothiocyanato ligand, and the N(4) atom of imidazole. Distortions from the ideal octahedral angles arise, in part, as a result of the conformation of the salen ligand and are similar to those found in related systems (Calligaris *et al* 1972). The central ethylenediamine FeN₂C₂ ring adopts the 'gauche' (meso) conformation while the two halves of the salen ligand are essentially coplanar. The Fe-salen geometry is very similar to that recently observed in the high-spin complex [Fe(salen)(imd)₂](PF₆) for which we have noted a possible relationship between conformation and spin-state (Kennedy *et al* 1987). Some pertinent comparisons with this PF₆⁻ salt (the latter in parentheses) are: angles O(2)-Fe-O(1) = 107.9(2)° (107.2(2)°), O(1)-Fe-N(2) = 87.1(2)° (88.2(2)°), N(2)-Fe-N(3) = 76.8(2)° (76.8(2)°); distances N(2) ... N(3) = 2.628(8) Å (2.652(9) Å), O(1) ... O(2) = 3.101(7) Å (3.064(7) Å). The iron atom in complex **I** sits in the plane of the salen donor atoms; the mean planes and displacements therefrom are given in table 5.

It has been noted in related studies (Kennedy *et al* 1985, 1987; Calligaris *et al* 1972) that the length of the metal-imine bond is sensitive to the spin state of the metal ion. The metal ion in high-spin complexes form longer M-N bonds than in corresponding low-spin complexes. The Fe^{III}-N(imine) distances in high-spin complexes are normally in the range 2.05-2.15 Å, and in low-spin complexes in the range 1.90-1.96 Å. The Fe-N(2) and Fe-N(3) distances found for **I** are in the range

Table 3. Selected bond lengths (Å) in **I**. (Atoms marked with an asterisk refer to the second crystallographically distinct molecule in the asymmetric unit.)

O(1)–Fe	1.928(4)	O(1')–Fe'	1.926(4)
O(2)–Fe	1.907(4)	O(2')–Fe'	1.888(4)
N(2)–Fe	2.125(5)	N(2')–Fe'	2.093(5)
N(3)–Fe	2.108(5)	N(3')–Fe'	2.091(5)
N(1)–Fe	2.085(5)	N(1')–Fe'	2.106(6)
N(4)–Fe	2.149(5)	N(4')–Fe'	2.145(5)
C(2)–O(1)	1.345(8)	C(2')–O(1')	1.343(7)
C(17)–O(2)	1.344(8)	C(17')–O(2')	1.322(7)
C(7)–C(8)	1.445(10)	C(7')–C(8')	1.471(9)
C(12)–C(11)	1.450(9)	C(12')–C(11')	1.454(9)
C(8)–N(2)	1.284(9)	C(8')–N(2')	1.280(8)
C(11)–N(3)	1.299(9)	C(11')–N(3')	1.308(8)
N(2)–C(9)	1.478(9)	N(2')–C(9')	1.476(8)
N(3)–C(10)	1.481(8)	N(3')–C(10')	1.478(9)
C(9)–C(10)	1.536(11)	C(9')–C(10')	1.553(11)
N(1)–C(1)	1.149(8)	N(1')–C(1')	1.150(8)
C(1)–S(1)	1.633(6)	C(1')–S(1')	1.625(6)
C(18)–N(4)	1.331(8)	C(18')–N(4')	1.315(9)
C(18)–N(5)	1.371(9)	C(18')–N(5')	1.367(10)
C(19)–N(5)	1.370(10)	C(19')–N(5')	1.353(11)
C(19)–C(20)	1.375(11)	C(19')–C(20')	1.343(14)
C(20)–N(4)	1.388(10)	C(20')–N(4')	1.374(9)
C–O	1.426(13)		

Table 4. Selected bond angles (in degrees) for **I**. (Atoms marked with an asterisk refer to the second crystallographically distinct molecule in the asymmetric unit.)

O(2)–Fe–O(1)	107.9(2)	O(2')–Fe'–O(1')	103.4(2)
O(2)–Fe–N(3)	88.2(2)	O(2')–Fe'–N(3')	88.6(2)
N(3)–Fe–N(2)	76.8(2)	N(3')–Fe'–N(2')	78.1(2)
N(2)–Fe–O(1)	87.2(2)	N(2')–Fe'–O(1')	90.0(2)
N(2)–Fe–O(2)	164.4(2)	N(2')–Fe'–O(2')	166.6(2)
N(3)–Fe–O(1)	163.9(2)	N(3')–Fe'–O(1')	167.9(2)
N(4)–Fe–N(1)	177.8(2)	N(4')–Fe'–N(1')	178.4(2)
N(2)–C(8)–C(7)	124.2(6)	N(2')–C(8')–C(7')	124.7(6)
N(3)–C(11)–C(12)	123.1(6)	N(3')–C(11')–C(12')	123.4(6)
C(2)–C(7)–C(8)	125.3(6)	C(2')–C(7')–C(8')	124.8(6)
C(11)–C(12)–C(17)	125.4(6)	C(11')–C(12')–C(17')	124.9(5)
C(7)–C(2)–O(1)	122.2(6)	C(7')–C(2')–O(1')	124.0(6)
C(12)–C(17)–O(2)	123.6(5)	C(12')–C(17')–O(2')	122.6(5)
C(2)–O(1)–Fe	132.1(3)	C(2')–O(1')–Fe'	130.1(4)
C(17)–O(2)–Fe	129.5(3)	C(17')–O(2')–Fe'	130.6(4)
C(8)–N(2)–C(9)	118.7(5)	C(8')–N(2')–C(9')	118.3(5)
C(11)–N(3)–C(10)	117.6(5)	C(11')–N(3')–C(10')	118.9(5)
N(2)–C(9)–C(10)	106.8(5)	N(2')–C(9')–C(10')	106.8(6)
N(3)–C(10)–C(9)	105.6(5)	N(3')–C(10')–C(9')	107.3(5)
Fe–N(4)–C(18)	124.4(4)	Fe'–N(4')–C(18')	126.0(4)
Fe–N(4)–C(20)	127.9(4)	Fe'–N(4')–C(20')	127.4(5)
Fe–N(1)–C(1)	159.0(5)	Fe'–N(1')–C(1')	161.2(5)
N(1)–C(1)–S(1)	179.2(6)	N(1')–C(1')–S(1')	179.4(6)

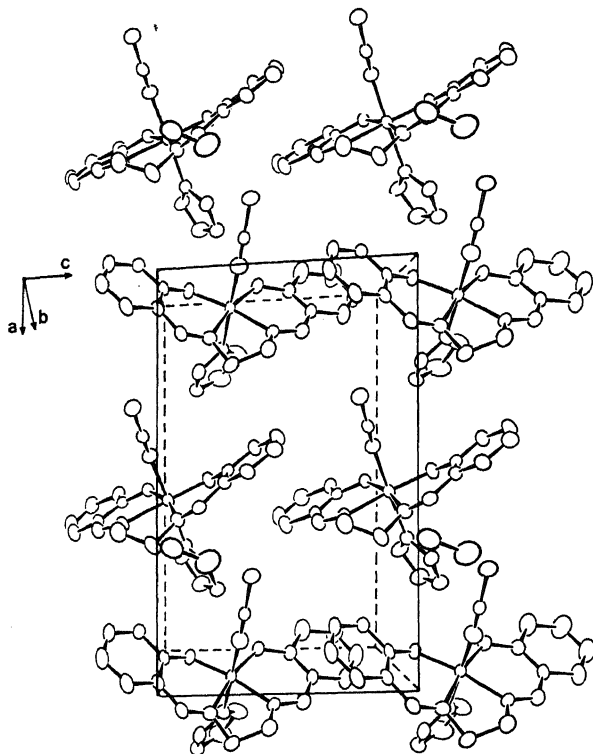


Figure 2. Crystal packing diagram for complex **I**.

Table 5. Mean planes in the two different molecules of (imd)Fe(salen)(NCS) of the asymmetric unit. Displacements in Å units.

<i>Molecule 1</i>	
Mean plane equation	$-0.041X - 0.033Y + 0.0007Z + 1 = 0$
"in-plane" atoms	Fe, 0; O(1), 0.025; O(2), -0.025; N(2), -0.028; N(3), 0.03
"out-of-plane" atoms	C(9), -0.346; C(10), 0.3
<i>Molecule 2</i>	
Mean plane equation	$-0.074X - 0.036Y - 0.029Z + 1 = 0$
"in-plane" atoms	Fe', 0.016; O(1'), 0.036; O(2'), -0.048; N(2'), -0.052; N(3'), 0.046
"out-of-plane" atoms	C(9'), -0.416; C(10'), 0.31

2.09–2.15 Å which is indicative of a high-spin ground state for Fe^{III} in the complex and consistent with the spectroscopic and magnetic data (see below). This compares with corresponding Fe–N distances of 1.90–1.92 Å in the low-spin (low temperature) form of [(imd)₂Fe(salen)](ClO₄) (Kennedy 1984; Kennedy *et al* 1987).

The Fe–N(imidazole) distance of 2.149(5) Å is very similar to that observed in high-spin *bis*-imidazole Fe^{III} salen systems (Kennedy *et al* 1987) and in high-spin [(5Ph-imd)Fe(3MeO-salen)(H₂O)]BPh₄ (Kennedy *et al* 1985). The geometrical

features of the iron-isothiocyanate group are compared in table 6 with those for related Fe^{III} porphyrin complexes (Scheidt *et al* 1982; Geiger *et al* 1985). N–C and C–S distances are similar in all cases. The Fe–N distance for the lower-spin TPP complexes are notably shorter than for the two high-spin complexes. While the NCS moiety is linear as expected, the FeNC angle in **I** and in two forms of the TPP complex is somewhat bent. In the latter cases the non-linearity has been ascribed to packing interactions in the solid state. The same situation may apply in **I** although there do not appear to be any unusual intermolecular interactions other than those involving methanol and the salen group as described above. The related azido complex (Clearfield *et al* 1978), [(py)Co(acen)(N₃)], shows an even more acute Co–N–N angle of 116.9°, rather similar in magnitude to the Fe–N–C angle found in the ligand binding pocket of (NCS)-methemoglobin ($120 \pm 10^\circ$) (Korszun and Moffatt 1981).

3.2 Mössbauer effect, ESR spectra and magnetism

The zero-field Mössbauer spectrum of **I** measured between 4.2 and 300 K consists of a single asymmetrical doublet (figure 3). The values of the isomer shift and quadrupole splitting, obtained by fitting the spectra to two unconstrained Lorentzian lines are typical of high-spin iron(III) complexes (table 7) and are similar to the values observed in other six-coordinate high-spin Lewis base adducts of Fe(III)salen such as [Fe(3MeO-salen)(Ph-imd)(H₂O)]BPh₄ and [Fe(salen)(imd)₂]PF₆ (Kennedy *et al* 1985, 1987). At all temperatures the two lines have a difference in area of $\approx 10\%$ which increases only slightly on cooling and is

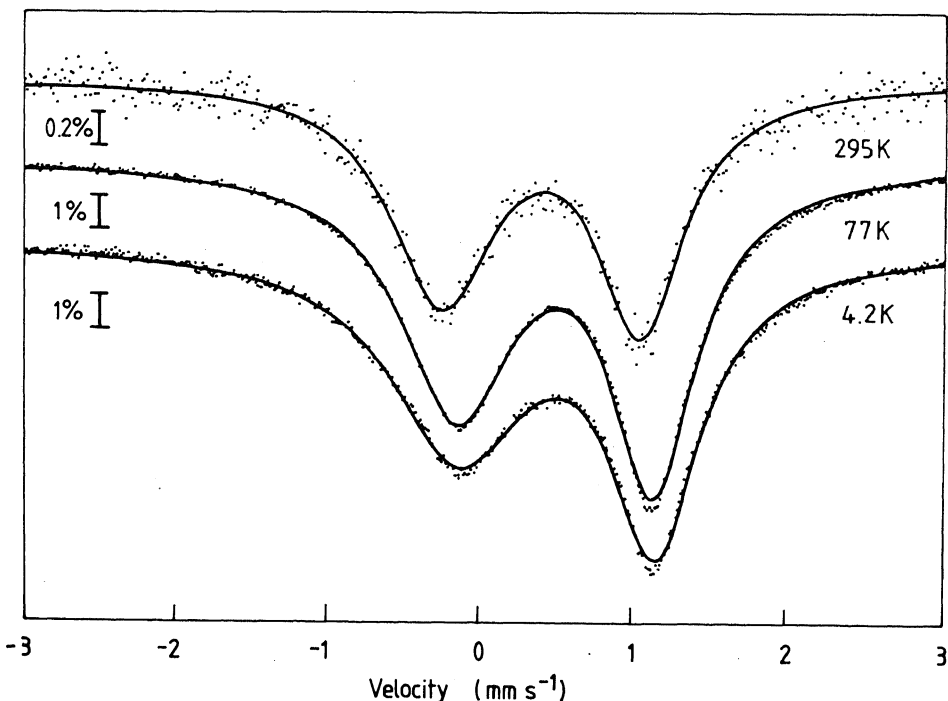


Figure 3. Mössbauer spectra of complex **I** in zero applied field at 295, 77 and 4.2 K.

Table 6. Fe-NCS geometry in [(imd)Fe(salen)(NCS)]0.5 MeOH I, and related porphyrin complexes at 295 K.

	<u>I</u>	[(py)Fe(OEP)(NCS)]	[(py)Fe(TPP)(NCS)]0.5 py	Site 1	[(py)Fe(TPP)(NCS)] Site 2
Spin state	5/2	5/2	"1/2"	$1/2 \rightleftharpoons 5/2$	5/2
Fe-N (Å)	2.085	2.031	1.942	1.91	1.97
N-C (Å)	1.149	1.153	1.144	-	-
C-S (Å)	1.633	1.626	1.606	-	-
NCS (°)	179.2	179.6	177.0	-	-
FeNC (°)	159.0	176.0	155.6	175	139
reference	this work	(Scheidt <i>et al</i> 1982)	(Scheidt <i>et al</i> 1982)	(Geiger <i>et al</i> 1985)	(Geiger <i>et al</i> 1985)

Table 7. Zero field Mössbauer parameters.

Complex	T(K)	δ^a (mms ⁻¹)	ΔE_Q (mms ⁻¹)	half-width ^b Γ_1, Γ_2	area ratio line 2/line 1	I_2/I_1^c
<u>I</u>	295	0.41	1.29	0.41, 0.33	0.90	1.1
	77	0.50	1.29	0.45, 0.33	0.93	1.28
	4.2	0.51	1.29	0.55, 0.35	0.91	1.40
<u>II</u> (fit 1)	295	0.38	0.92	0.56, 0.56	d	1.0
	77	0.52	0.93	0.59, 0.47	d	1.1
	4.2	0.48	0.98	0.49, 0.48	d	1.57
<u>II</u> (fit 2)	295	0.38	0.92	0.56, 0.56	d	1.0
	77	0.50	0.91	0.48, 0.51	d	1.29
		0.36 ^e	2.67	0.37, 0.37		
	4.2	0.49	0.89	0.40, 0.41	d	1.55
		0.36 ^e	2.67	0.38, 0.38		

^a relative to Fe. ^b half-width at half-height in mm s⁻¹ for line 1 of the doublet at lower velocity and line 2 at higher velocity. ^c ratio of intensities. ^d area ratio not meaningful because of contribution of Gaussian base line curve (see text). ^e second weak doublet constrained to these values.

thought to arise from the Goldanskii-Karyagin effect (Karyagin 1963; Goldanskii *et al* 1968). The increase in the isomer shift at low temperatures is probably due to the second-order Doppler shift.

The increase in asymmetry of the peak intensities at lower temperatures can be explained in terms of spin-spin relaxation effects in a system where the $M_s = \pm 5/2$ Kramers doublet lies lowest (i.e. D , the axial ZFS parameter, is negative, Buckley 1971). When the $|\pm 5/2\rangle$ states lie lowest a quadrupole doublet will be observed if the rate of spin-spin relaxation, τ , is slower than ω_i^{-1} (where ω_i is the angular nuclear harmonic precession frequency). The spin-spin relaxation rate is expected to be slower at 4.2 K than at higher temperatures, since for spin flips induced by dipolar coupling between molecules, transitions between the $|+5/2\rangle$ and $|-5/2\rangle$ states are forbidden. The slowly relaxing $|\pm 5/2\rangle$ ground state results in preferential broadening of one line of the quadrupole doublet. At higher temperatures where the $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ doublets are also populated the asymmetry in peak height is expected to reach a minimum. If τ was greater than ω_i^{-1} , or even comparable with it at 4.2 K then magnetic hyperfine would be expected.

The Mössbauer spectra for the azide complex II at various temperatures are shown in figure 4. The spectra were less straightforward to fit than those for I since they are not fully relaxed and therefore a broad Gaussian baseline component was included in the fit. Also there is a weak low velocity shoulder present in the 4.2 K and 77 K spectra arising, possibly, from trace quantities of a low-spin species. The parameters for two separate fits are given in table 7. In both cases the isomer shifts and quadrupole splittings due to II are very similar. The δ values are similar to those in I while the ΔE_Q values are lower, probably because of a more symmetrical arrangement of the N₄O₂ donor set in the azido-complex. Fit 1 used two unconstrained Lorentzian lines together with a Gaussian base curve contributing about 50% of the area. While this fit reproduced the majority of the line-shape quite well it did not, of course, fit the shoulder at low velocity. The increase in

intensity asymmetry as the temperature decreased followed the same pattern as in **I**. In fit 2 a second doublet was included with parameters constrained to the values observed for low-spin *bis*-imidazole Fe^{III} -salen species (Kennedy *et al* 1987). This improved the overall fit of the lineshapes. Again, a broad Gaussian baseline curve was incorporated and contributed 33% (at 77 K) to 41% (at 4.2 K) of the area. The second (low-spin) doublet contributed only about 5% of the total area.

Despite the complexities of the line-fitting the temperature dependence of the Mössbauer spectra of **II** can be explained in a similar manner to that given for **I** and it appears that D is also negative in this complex. The sign of D found in the present compounds is the opposite to that observed in most other well characterized six-coordinate Fe^{III} Schiff-base complexes such as $[\text{Fe}(\text{salen})(\text{imd})_2]\text{PF}_6$ ($D = 0.6 \text{ cm}^{-1}$), $[\text{Fe}(3\text{MeO-salen})(5\text{-Ph-imd})(\text{H}_2\text{O})]\text{BPh}_4$ ($D = 5.0 \text{ cm}^{-1}$) and the parent dimer $[\text{Fe}(\text{salen})\text{Cl}]_2$ (Buckley *et al* 1970). However, some five-coordinate *bis*-bidentate Schiff-base complexes such as $[\text{Fe}(\text{sal-N-ptolyl})_2\text{Cl}]$ also appear to have the $|\pm 5/2\rangle$ state lowest (Buckley 1971). The exact nature and magnitude of the ground state splitting in these types of compounds is apparently critically dependent on the number *and* nature of the coordinated ligands. This is well demonstrated in the seven-coordinate complexes $[\text{Fe}(\text{N}_5)\text{X}_2]$, ($\text{X} = \text{SCN}^-$, N_3^- ; N_5 is a pentadentate macrocycle) where the sign of D changes from positive for $\text{X} = \text{SCN}^-$ to negative for $\text{X} = \text{N}_3^-$ (Scoville and Reiff 1983).

The temperature dependence of the magnetic moment for $[(\text{imd})\text{Fe}(\text{salen})(\text{NCS})]$ is shown in figure 5 and is characteristic of a high-spin Fe^{III} system

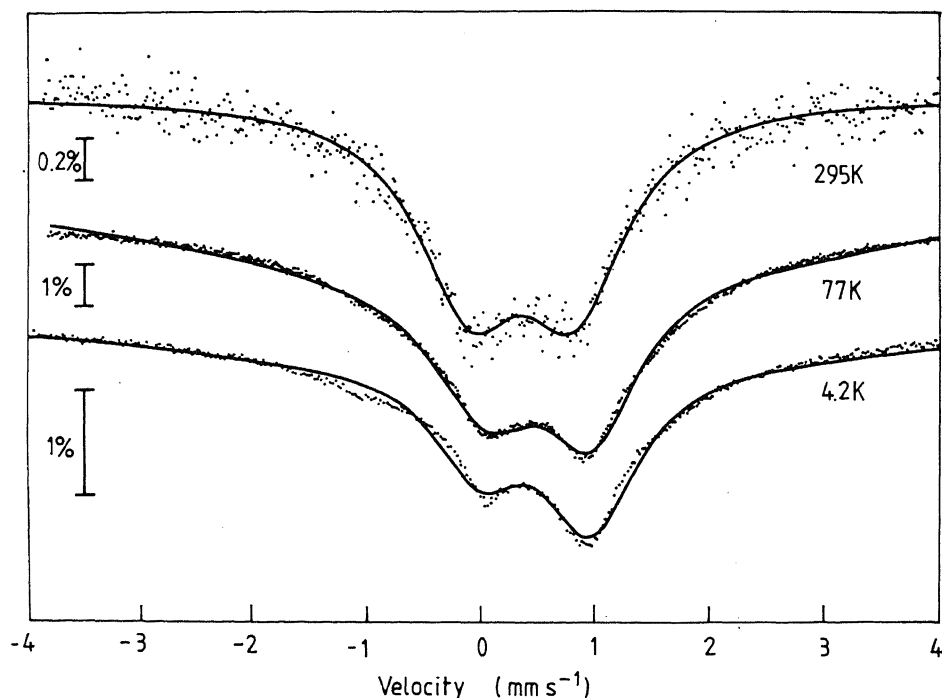


Figure 4. Mössbauer spectra of complex **II** in zero applied field at 295, 77 and 4.2 K. The solid lines represent fit 1 described in the text.

displaying appreciable ZFS. Thus μ_{Fe} remains constant at 5.9 B.M. above 20 K while below this it decreases rapidly to 5.3 B.M. at 4.2 K. Since the molecular symmetry of **I**, shown in figure 1 is clearly less than axial, the susceptibility data were fitted to the rhombic spin Hamiltonian

$$\mathcal{H} = g\beta\hat{H}\cdot\hat{S} + D[\hat{S}_z^2 - 1/3S(S+1)] + E(\hat{S}_x^2 - \hat{S}_y^2).$$

Susceptibilities were calculated by means of a spatial averaging technique at the experimental magnetic field using the thermodynamic expression (Marathe and Mitra 1974; Vermaas and Groeneveld 1974; Mitra 1982). As has been noted previously, powder susceptibilities are only sensitive to the size of D and are insensitive to its sign and to the size of any rhombic splitting (Mitra 1982; Berry *et al* 1983). With these limitations in mind, and the knowledge that the Mössbauer spectral data suggest D to be negative, the present data could be reproduced very well with $D = -2.4 \pm 0.2 \text{ cm}^{-1}$, $E = 0.6 \pm 0.2 \text{ cm}^{-1}$ and $g = 1.98 \pm 0.02$. It is interesting to note that there is no evidence for any weak exchange coupling via the H-bonded methanol network. This contrasts with the situation in $[\text{Fe}(\text{3-MeO-salen})(\text{5-Ph-imd})(\text{H}_2\text{O})]^+$ in which H-bonding to the bonded water molecule occurs between pairs of cations (Kennedy *et al* 1985). The temperature dependent susceptibilities of the azide complex, **II**, are similar to those shown in figure 5, although the low temperature decrease in μ_{Fe} is somewhat less indicating a smaller ZFS. Best-fit parameters of $D = -1.4 \pm 0.2 \text{ cm}^{-1}$, $E = 0.4 \pm 0.2 \text{ cm}^{-1}$ and $g = 2.00 \pm 0.01$ were obtained for **II**. There is no evidence from the μ_{Fe}/T data for

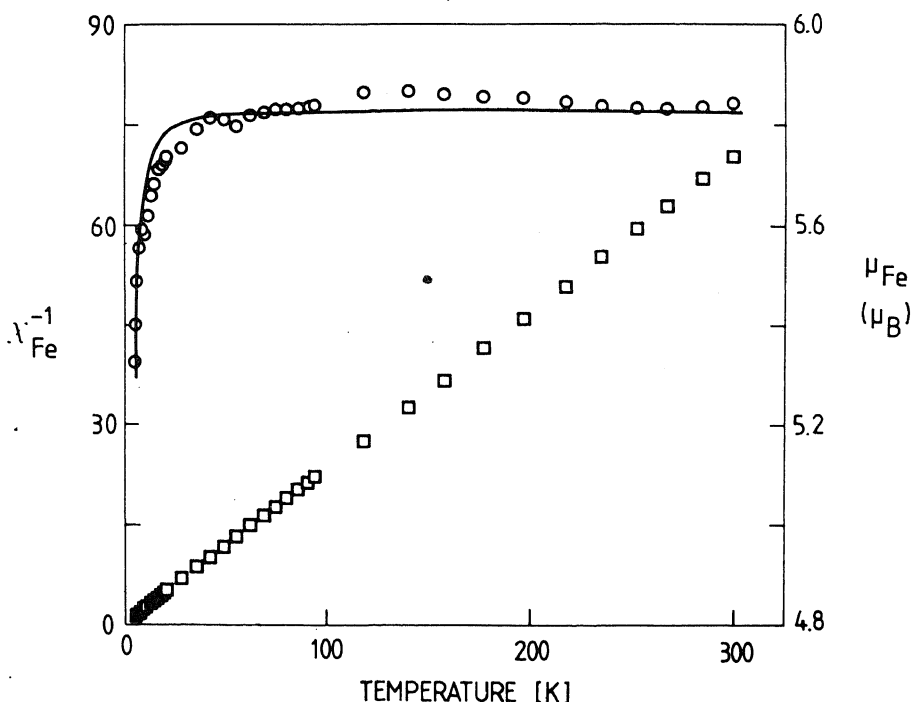


Figure 5. Magnetic moment (○) and reciprocal susceptibility (□) (per iron) versus temperature for complex **I**. The solid line represents the best fit of the data to the spin Hamiltonian in the text.

the presence of small quantities of an $S = 1/2$ contaminant, but this would be very hard to detect.

In principle ESR spectroscopy should provide a much more sensitive probe for rhombic splitting of the 6A_1 ground state than powder susceptibilities. A polycrystalline sample of II at 80 K showed a single broad resonance at $g \sim 4.4$ (figure 6). The origin of such a line has been discussed elsewhere (Peisach and Blumberg 1971; Oosterhuis 1974) and in the present case can be thought to be due to appreciable rhombic splitting of the 6A_1 state with the ratio of E/D approaching $1/3$ in reasonable agreement with the magnetic data. There was no evidence for any low-spin signals at $g \sim 2$, which might be expected in view of the Mössbauer spectra. However a low concentration of such species might be difficult to detect in the powder ESR spectrum. Under identical conditions, the ESR spectrum of a neat powdered sample of I surprisingly shows a single resonance at $g \sim 2.1$. In frozen ethanol/chloroform glass, the spectrum of I does, however, show a strong line at

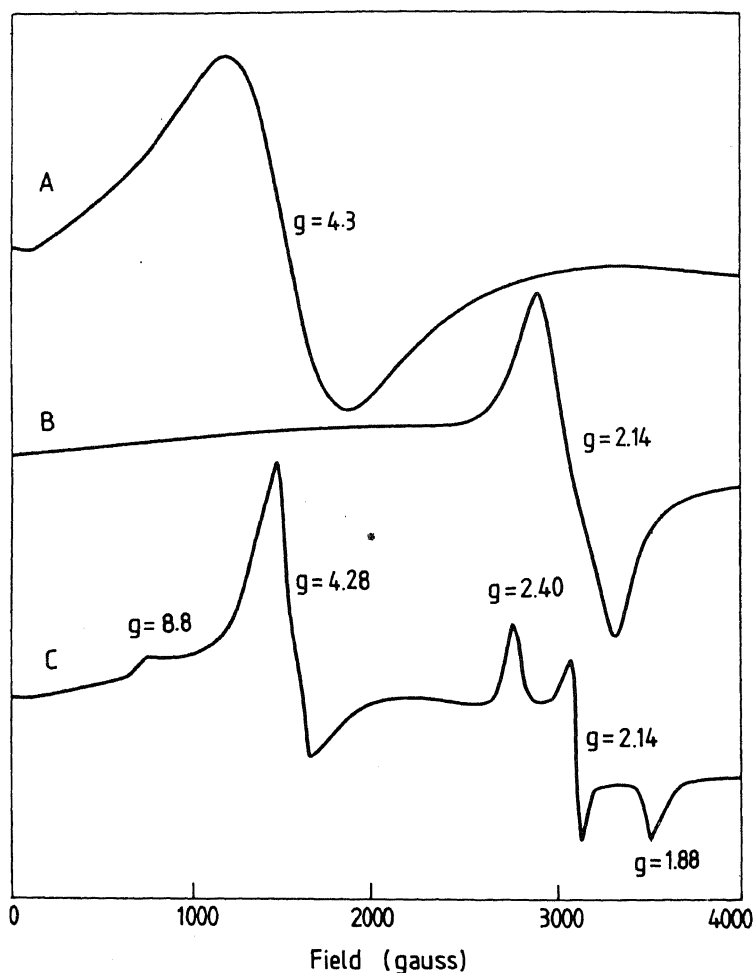


Figure 6. X-band ESR spectra at 80 K: (A) powder sample of II, (B) powder sample of I, (C) frozen glass (EtOH/ CHCl_3) spectrum of I. The three lines at $g \sim 2$ are due to low-spin *bis*-imidazole species; see text.

$g = 4.3$ with somewhat weaker lines at $g = 8.84, 2.40, 2.14$ and 1.88 . The lines at $g = 8.84$ and 4.3 can be attributed to high-spin Fe^{III} with $E/D \sim 1/3$ and are assigned to $[(\text{imd})\text{Fe}(\text{salen})(\text{NCS})]$. The three lines near $g = 2$ in the frozen glass are due to a low-spin Fe^{III} complex which is formed in solution by the partial dissociation of the mono-adduct and subsequent formation of small amounts of the low-spin *bis*-imidazole adduct, i.e. $2[(\text{imd})\text{Fe}(\text{salen})(\text{NCS})] \rightleftharpoons [(\text{imd})_2\text{Fe}(\text{salen})]\text{NCS} + \text{Fe}(\text{salen})(\text{NCS})$. Under similar conditions a sample of $[\text{Fe}(\text{salen})(\text{NCS})]$ was ESR silent presumably because of exchange coupling between dimeric units as in $[\text{Fe}(\text{salen})\text{Cl}]_2$. It is not clear why the neat solid spectrum of **I** should show a resonance at $g = 2.1$ and be different from that of **II**. Since the glass spectrum shows the $g = 4.3$ signal it seems likely that exchange effects rather than any fundamental difference in ligand-field splittings are causing the differences in the spectra. Somewhat related effects were observed in the high-spin complexes $[\text{Fe}(\text{R-salen})(\text{H}_2\text{O})\text{L}]\text{BPh}_4$, although the powder spectra in these cases tended to show lines at very low fields (Kennedy *et al* 1985). The sign of D was also reversed compared to **I** and **II**.

Finally, it is interesting to contemplate the possible reasons for a change in the sign of D in **I** and **II** compared to the $[\text{Fe}(\text{R-salen})(\text{H}_2\text{O})(5\text{Ph-imd})]^+$ species (Kennedy *et al* 1985). Changes in the axial combination from $\{\text{H}_2\text{O}, 5\text{Ph-imd}\}$ (D positive) to $\{\text{NCS}^-, \text{imd}\}$ (D negative) would appear to be the dominant cause. NCS^- generally has a marginally larger Dq value than H_2O and has more π -bonding capability than H_2O . The $\text{Fe}-\text{N}(\text{CS})$ distance is shorter than the $\text{Fe}-\text{O}(\text{H}_2)$ distance while the $\text{Fe}-\text{N}(\text{imidazole})$ distances are the same. The in-plane $\text{Fe}-\text{O}$ and $\text{Fe}-\text{N}$ distances are slightly longer in **I** compared to $[\text{Fe}(\text{3MeO-salen})(\text{H}_2\text{O})(5\text{Ph-imd})]\text{BPh}_4$. All these effects presumably combine to reverse the order of the low-lying quartet state sub-levels (4A_2 or 4E in D_{4h}), which is responsible for the size and sign of ZFS of the 6A_1 ground state. In order to probe further into the subtleties of these electronic features, experimental determinations of single-crystal magnetism, high-field magnetization and applied-field Mössbauer spectra would be required (Mitra 1982; Berry *et al* 1983; Kennedy and Murray 1985). Unfortunately the direct observation of excited ligand-field levels via visible spectroscopy is not possible in Fe^{III} Schiff-base systems because of overlying charge-transfer bands. From the theoretical point of view an angular overlap analysis of the σ - and π -bonding effects of the axial and in-plane ligands would be worthwhile in relation to the ground state ZFS, but this remains a formidable problem for d^5 high-spin configurations (Gerloch 1979).

Acknowledgements

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Supplementary material: Listings of fractional atomic coordinates and anisotropic thermal parameters, all bond lengths and angles, and the observed and calculated structure factor tables are available at the editorial office and with the authors.

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Magnetic properties of some exchange coupled $[\text{Ni}(\text{mnt})_2]^-$ dimers

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Abstract. The metal dithiolenes exhibit interesting solid state properties owing to the presence of columnar crystallographic packing. Particularly, the *bis*(maleonitriledithiolato)-nickel(III) systems with a variety of organic and inorganic counter ions seem to possess low-dimensional magnetic interactions and charge-transfer properties. The metal chelates show strong alternation in their packing and result in reduced magnetic moments as a consequence of antiferromagnetic exchange coupling between the pairs. We have studied a few interesting dimers through x-ray structure and magnetic susceptibility measurements and the results are used to arrive at a correlation between the observed magnetic behaviour and the structure of the dimeric units.

Keywords. Exchange interaction; magnetic susceptibility; dimers.

1. Introduction

Metal dithiolene complexes show unique low-dimensional magnetic, electrical and optical properties (McCleverty 1968; Miller and Epstein 1976; Jacobs *et al* 1976; Isétt *et al* 1980; Miller 1982; Cooper *et al* 1983). This behaviour is due to the fact that these metal chelates possess an overall planar geometry allowing them to stack-up along a particular direction, which is an important requirement for a system to exhibit low-dimensional properties. In addition, they exhibit a number of characteristics which make them particularly attractive candidates as π -acceptor units in the formation of donor-acceptor compounds; they undergo reversible electron-transfer reactions to yield stable species; they possess species with sufficiently high electron affinity to remove an electron from a wide variety of organic donors and structural flexibility available via the changes in the central metal atom, ligand substituent and the counter ion, which can be varied in a systematic way to study the effect of molecular features on the solid state structure and properties.

A variety of Cu(II) and Ni(III) dithiolene complexes were made in order to understand the low-dimensional cooperative phenomena in their solid state and the effect of dimensionality of the exchange coupled network on the solid state properties like magnetic, electrical and optical (Manoharan *et al* 1981; Ramakrishna and Manoharan 1983; Ramakrishna *et al* 1983; Kuppusamy *et al* 1984a, b; Kuppusamy and Manoharan 1985a, b; Kuppusamy *et al* 1985a, b). Our primary emphasis was to deduce the nature and size of the various exchange interactions present in the system. We have shown in a number of cases that EPR in conjunction with magnetic susceptibility measurements can be very useful in extracting these parameters. Though EPR is a more sensitive tool for weakly

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exchange coupled systems ($|J| < 1 \text{ cm}^{-1}$) the magnetic susceptibility measurements can be used for strongly exchange coupled systems. In this paper we present and discuss some of our magnetic susceptibility results on a few strongly exchange coupled $\text{Ni}(\text{mnt})_2^-$ dimers.

2. Experimental

2.1 Preparation of compounds

Tetra-*n*-butylammonium bis(maleonitriledithiolato) nickelate(III), $[\text{NBu}_4][\text{Ni}(\text{mnt})_2]$ was prepared according to the reported (Davison and Holm 1971) procedure. N-methyl-phenazinium methosulphate, $\text{NMP}^+\text{CH}_3\text{SO}_4^-$ (Aldrich Chemical Co.), was dissolved in acetonitrile and treated with $[\text{NBu}_4]^+[\text{Ni}(\text{mnt})_2]^-$ in the same solvent. The resulting dark solution was filtered and cooled in the refrigerator for 24 hours. The black needles were collected on a filter, washed with ice-cold acetonitrile and dried in air. The yield was 60%.

Analysis: Found (%): C 46.98; H 2.3; N 15.70; Calc. (%): C 47.23; H 2.08; N 15.74.

2.2 Magnetic susceptibility measurements

Magnetic susceptibility measurements were carried out on the powder samples at a field of 18.94 kG using PAR Vibrating Sample Magnetometer in the temperature range 4.2–340 K. The error in temperature was ± 0.5 K while that in susceptibility was within 2%. The measured susceptibility values were corrected for underlying diamagnetism using Pascal's constants.

3. Magnetic susceptibility of exchange coupled dimers

Considerable progress has been made towards the understanding of the nature of magnetic interactions in low-dimensional systems (de Jongh and Miedema 1974). The spin Hamiltonian in the case of a low-dimensional system is given by

$$\mathcal{H} = \sum_{i=1}^{N/2} (J_1 S_{2i} S_{2i-1} + J_2 S_{2i} S_{2i+1}), \quad (1)$$

where J_1 and J_2 are the exchange coupling constants of a spin at $2i$, to its neighbouring spins at $(2i-1)$ and $(2i+1)$, respectively. The ratio J_2/J_1 , say α , is termed as the alternation parameter and it defines the dimensionality of the exchange coupled net work. For $\alpha = 1$ we have uniform coupling on both sides and hence the system is said to be 'uniform' or 'linear' chain with dimensionality unity. A zero value to alternation parameter indicates that the reference spin is coupled to only one of its neighbours and this is analogous to the dimerization of the spin system leading to exchange coupled dimers. The dimensionality in such a case would be zero. For values of α between 0 and 1, one has the 'alternating' chains with differing J_1 and J_2 .

The case of uniform exchange between spins along the chain has been studied mainly by Bonner and Fisher (1964), and Bulaevskii (1962), while the case of non-uniform or alternating exchange along the chain has been considered by Bulaevskii (1969) and Duffy and Baar (1968). The dimeric model also has been studied and reviewed extensively (Hatfield 1979). Using the Van Vleck (1932) expression for susceptibility the temperature dependence of the molar susceptibility for a system of doublet spins coupled into pairs is given by

$$\chi_M = \frac{Ng^2\beta^2}{3kT} [1 + \frac{1}{3} \exp(-2J/kT)]^{-1} + N\alpha + \chi_M^{\text{dia}}, \quad (2)$$

where $2J$ is the singlet-triplet separation, g is the effective average splitting factor, $N\alpha$ is the temperature independent paramagnetism (TIP) and χ_M^{dia} is the molar diamagnetic susceptibility. This expression, often referred to as the Bleaney-Bowers formula takes into account only the intradimeric interaction ($\alpha = 0$). For systems having significant interdimeric exchange contribution, a molecular field correction term is usually included to the Bleaney-Bowers formula as given by

$$\chi_M^{\text{corr.}} = \chi_M^{\text{BB}} / (1 - 2z J' \chi_M^{\text{BB}} / Ng^2\beta^2), \quad (3)$$

where χ_M^{BB} is the molar susceptibility of an isolated dimer of $S = \frac{1}{2}$ spins, J' is the interdimer exchange coupling constant and z is the number of nearest neighbours excluding the one to which the reference spin is strongly exchange coupled.

The interdimer interactions can also be included by using the following analytical expression developed by Hatfield and coworkers (Hatfield 1981; Hatfield *et al* 1982):

$$\chi_M = \frac{Ng^2\beta^2}{kT} \left[\frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3} \right], \quad (4)$$

where $x = J/kT$. The parameters A to F are defined as follows:

$$A = 0.25,$$

$$B = -0.12587 + 0.22752\alpha,$$

$$C = 0.019111 - 0.13307\alpha + 0.509\alpha^2 - 1.3167\alpha^3 + 1.0081\alpha^4,$$

$$D = 0.10772 + 1.4192\alpha,$$

$$E = -0.0028521 - 0.42346\alpha + 2.1953\alpha^2 - 0.82412\alpha^3,$$

$$F = 0.37754 - 0.067022\alpha + 5.9805\alpha^2 - 2.1678\alpha^3 + 15.838\alpha^4.$$

In the above expressions α is the alternation parameter as defined in (1) and the expressions are valid for $0 < \alpha < 0.4$. By measuring the molar susceptibility as a function of temperature and by fitting the data into (2), (3) or (4) one can get J , g and α with fair precision.

4. Structure of $\text{Ni}(\text{mnt})_2^-$ dimers

The $\text{Ni}(\text{mnt})_2^-$ systems generally exhibit two types of crystallographic packing. In the first type the metal chelate anions stack among themselves uniformly with

identical Ni-Ni distances along the stack direction giving rise to a linear (1D) chain system (Manoharan *et al* 1981; Ramakrishna and Manoharan 1983). A typical uniform chain packing is shown in figure 1. Such linear chain systems have been shown to have J values in the order of a few cm^{-1} or less. In the second type of structure (Fritchie 1966; Kobayashi and Sasaki 1977; Mahadevan *et al* 1983; Kuppusamy *et al* 1985a) there is an alternation of the interplanar spacing and hence alternating Ni-Ni distances along the stack direction, with varying degree of alternation. This alternation invariably results in dimerisation of the anions along the stack direction and this occurs involving the metal ions bridging to one of the sulphur atoms of the other anion of the same dimer. An example is shown in figure 2. The Ni . . . S (bridging, out-of-plane) distances range from 3.45 Å to 4 Å compared to the Ni-S (in-plane) distance ~ 2.15 Å.

The system $[\text{NMP}]^+[\text{Ni}(\text{mnt})_2]^-$ has an alternating type of stack (Kuppusamy *et al* 1985a). A projection of the packing arrangement onto the ab plane of the triclinic unit cell is shown in figure 3. The Ni atom has an approximate square-planar configuration with all the four Ni-S distances equal within experimental error. The average Ni-S distance within a chelate is 2.138 Å while that of Ni . . . S (out-of-plane) is 4.0 Å. The Ni-Ni contact within the dimer is 4.16 Å and that between two dimers is 7.87 Å. Hence the packing can be best described as dimeric with the dimers stacked along the a -axis of the unit cell.

Figure 4 shows the perpendicular projection of one anion onto the plane of the other anion of the same dimer. The interplanar distance between the two chelate planes is 3.58 Å. The compounds $[\text{Net}_4][\text{Ni}(\text{mnt})_2]$ (Kobayashi and Sasaki 1977) and $[\text{N}(\text{Ph})_3\text{Me}][\text{Ni}(\text{mnt})_2]$ (Fritchie 1966) also have been reported to have a similar packing, though the Ni-Ni alternations along the stack axis are not quite different. $[\text{NBu}_4][\text{Ni}(\text{mnt})_2]$ is structurally isomorphous to $[\text{NBu}_4][\text{Cu}(\text{mnt})_2]$, whose structure is known (Forrester *et al* 1964). A projection of the structure onto

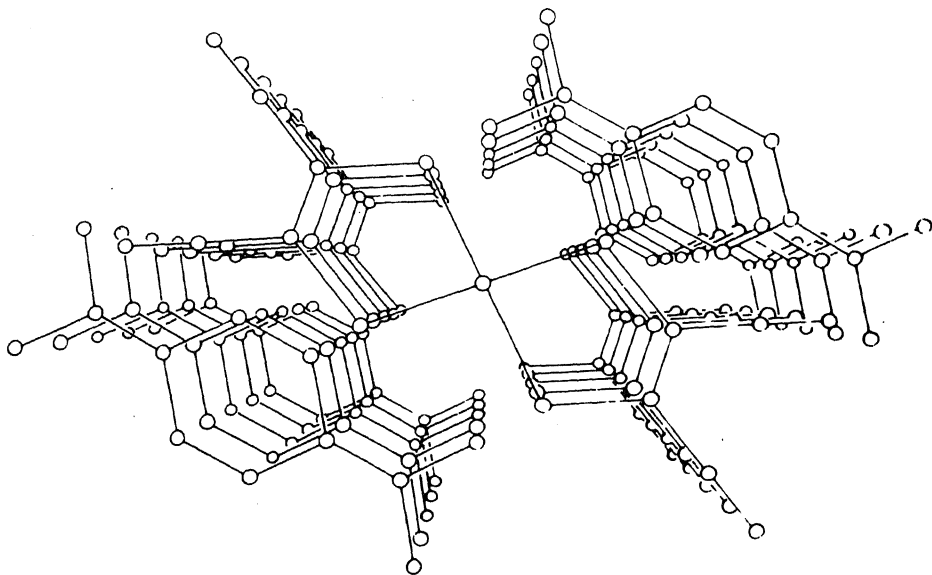


Figure 1. An example of uniform stack: $\text{TMPD}^+[\text{Ni}(\text{mnt})_2]^-$.

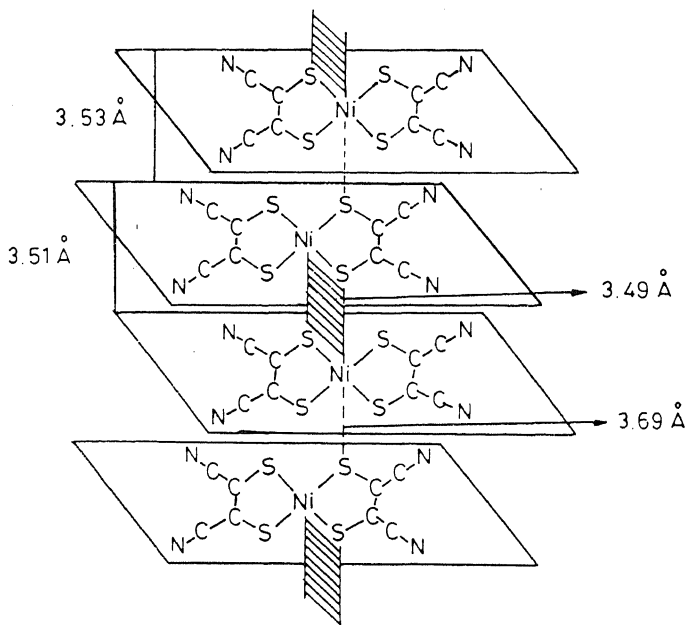


Figure 2. The anion stack of $\text{NEt}_4\text{Ni}(\text{mnt})_2$ showing the alternation in the Ni-S overlaps.

the ab plane in figure 5a shows the presence of $[\text{Cu}(\text{mnt})_2]^-$ dimers along the a -axis of the monoclinic lattice. Also shown in figure 5b is a projection of the pair as viewed down the stack axis. The Cu atoms in this structure have nearest Cu neighbours at 4.026 Å and 4.431 Å corresponding to respectively within the dimer and between the dimers.

5. Results and discussion

5.1 Magnetic susceptibility of $[\text{NMP}][\text{Ni}(\text{mnt})_2]$

All the alternating type $\text{Ni}(\text{mnt})_2^-$ systems show reduced magnetic moments (1.1 to 1.4 BM) at room temperature indicating the presence of antiferromagnetic coupling leading to a singlet ground state with a corresponding low-lying, thermally accessible triplet excited state. The temperature dependence of the paramagnetic susceptibility of $[\text{NMP}][\text{Ni}(\text{mnt})_2]$ is shown in figure 6. A broad maximum characteristic of low-dimensional antiferromagnetic coupling is seen around 210 K. A least squares minimization procedure with an error function F of the form,

$$F(J, g, N\alpha) = \sum_i (\chi_i^{\text{cal}} - \chi_i^{\text{obs}})^2 / (\chi_i^{\text{cal}})^2, \quad (4)$$

was used with J , g and $N\alpha$ as variable parameters. The best fit was obtained for the data in the temperature range 90–340 K by using expressions (2) and (4) for

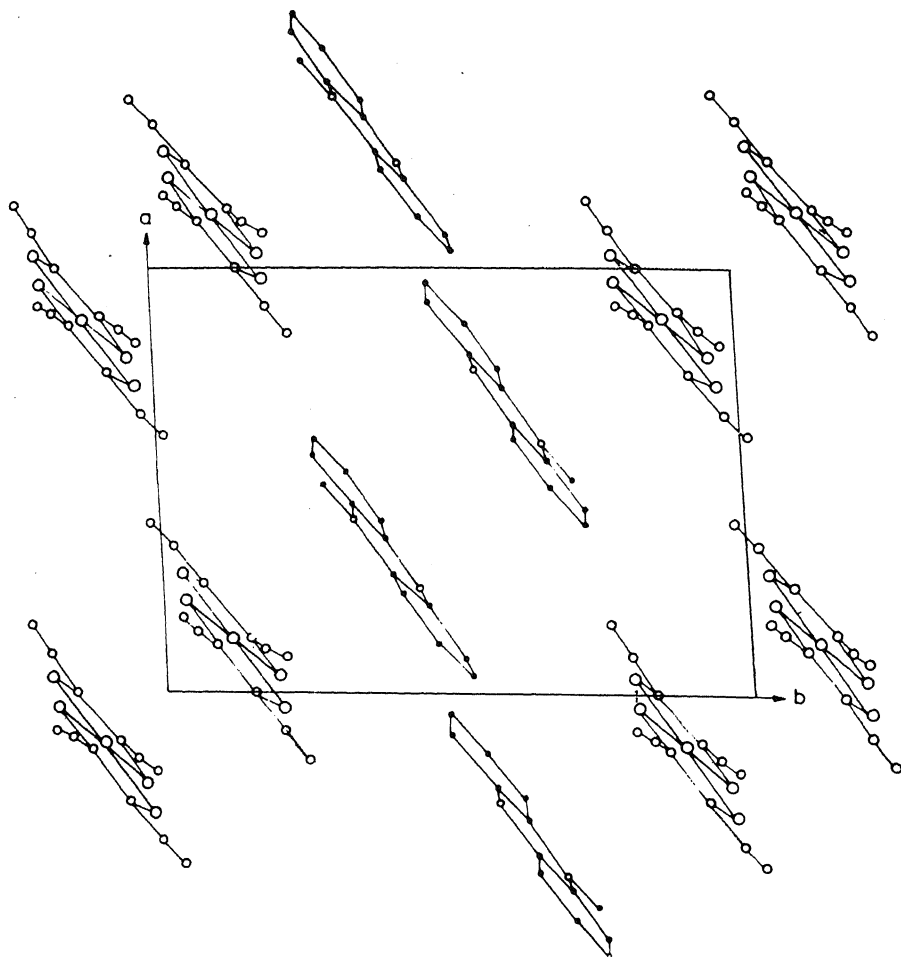


Figure 3. Projection of the packing arrangement in $[\text{NMP}] [\text{Ni}(\text{mnt})_2]$ onto the ab plane.

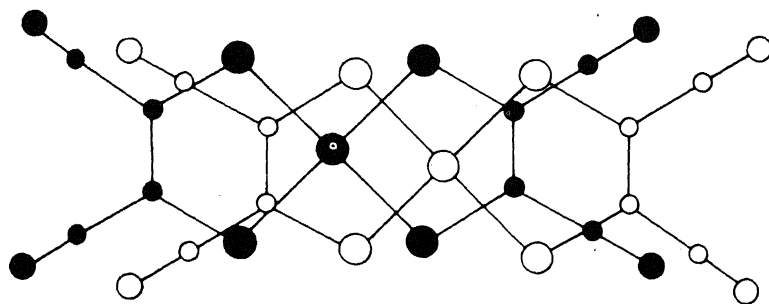


Figure 4. A perpendicular projection of one anion onto the plane of the other anion of $[\text{NMP}] [\text{Ni}(\text{mnt})_2]$.

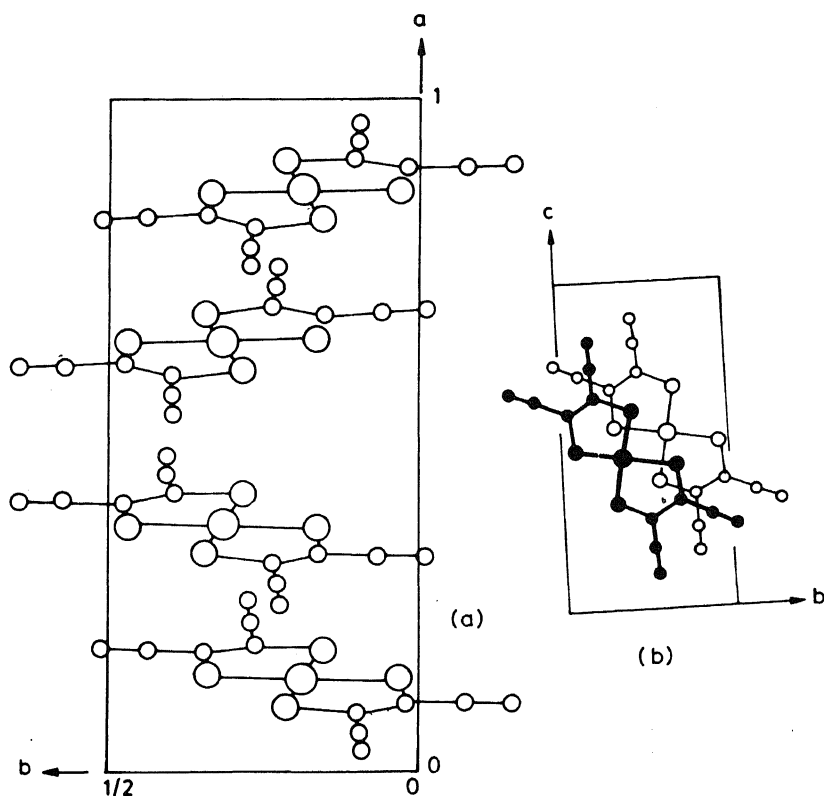


Figure 5. (a) A projection down the c -axis showing the $[\text{Cu}(\text{mnt})_2]^-$ anions from the side (b) A projection down the a -axis showing the $[\text{Cu}(\text{mnt})_2]^-$ dimer as viewed down the stack axis.

$2J = -241 \pm 2 \text{ cm}^{-1}$, $g = 2.061 \pm 0.002$ and $N\alpha = 206 \pm 5 \times 10^{-6} \text{ emu/mole}$. The singlet-triplet separation ($2J$, -241 cm^{-1}) is in the range expected for similar antiferromagnetically coupled $\text{Ni}(\text{mnt})_2^-$ dimers (Weiher *et al* 1964).

Below 90 K an increase in susceptibility is noted (figure 6) contrary to the expectation that it must drop to a constant value ($N\alpha$) at lower temperatures in the case of antiferromagnetic coupling. Sometimes such an increase is attributed to the presence of Curie type (monomeric) impurities and due allowance is then given for their contributions at higher temperatures before interpreting the data. However, in the present case, the plot of $(\log \chi)$ vs $(\log T)$ as seen in figure 7 shows a power-law behaviour of χ on T as

$$\chi = A T^{-\alpha}$$

or

$$\log(\chi) = \log(A) - \alpha \log(T), \quad (5)$$

with $\alpha = 0.85$. This clearly rules out the presence of monomeric impurities, for which α must have been unity.

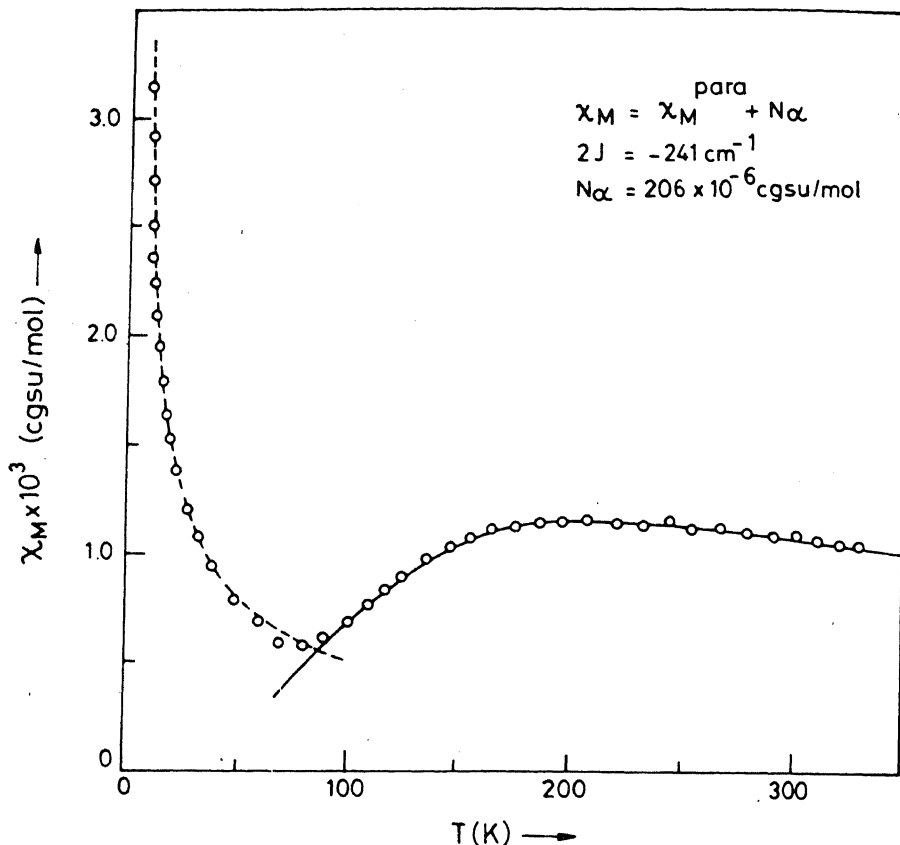


Figure 6. Temperature variation of χ_M^{para} of [NMP] [Ni(mnt)₂]. The solid line above 90 K represents the theoretical susceptibility calculated from (2) while that below 70 K represents the susceptibility calculated by using the ECP model (7).

The power-law divergence has already been recognised in the case of uniform as well as alternating chains (Bulaevskii 1962; Bondeson and Soos 1980) as a characteristic property of the system. The occurrence of chemical or packing defects is quite general in low-dimensional systems and can have drastic consequences on the magnetic and transport properties. Finite chain effects produce divergent susceptibilities associated with odd length segments and the susceptibility deviates from Curie law as shown by (5), with α ranging between 0.72 and 0.89. Bulaevskii (1962) and Bondeson and Soos (1980) have studied this in detail based on the 'Random exchange in Heisenberg antiferromagnetic chains (REHAC)' model.

Tippie and Clark (1981) have proposed the 'exchange coupled pair (ECP)' model for random exchanges in alternating chains. In their model the system is supposed to be having a set of independent exchange-coupled pairs with the value of J distributed randomly with a probability function $P(J)$ given by

$$P(J) = AJ^{-\alpha}, \quad (6)$$

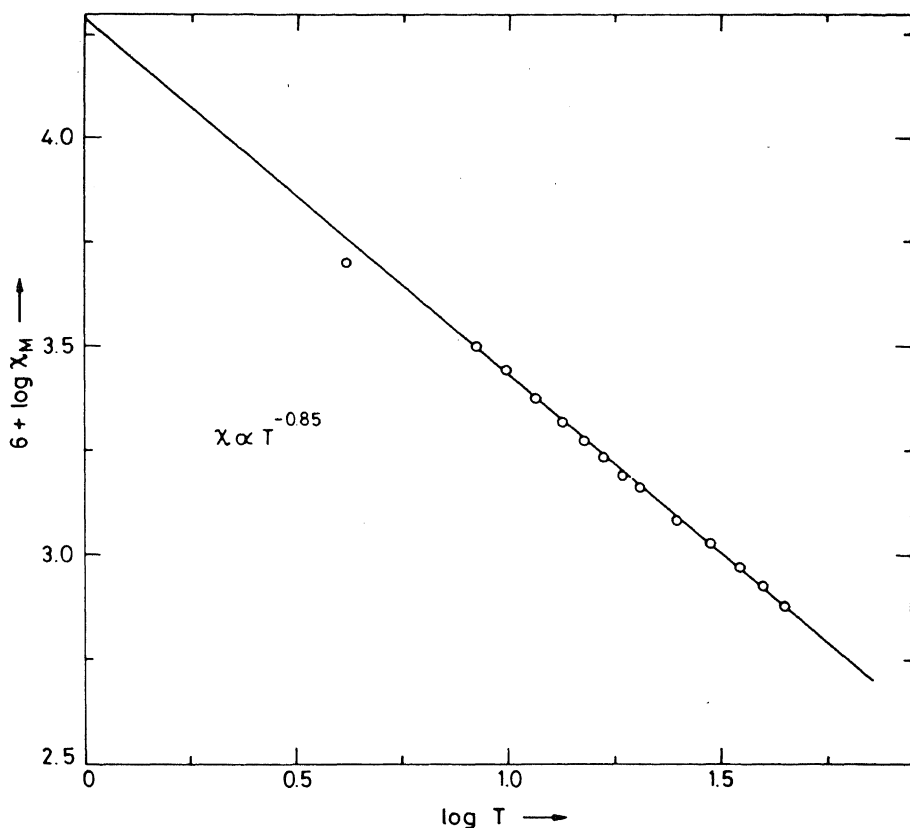


Figure 7. Plot of $\log \chi$ vs $\log T$ showing the power-law divergence with $\alpha = 0.85$.

where A and α are constants, $P(J)$ is normalised by introducing a cut-off at J_0 , the maximum J which occurs between the spin pairs at their minimum separation. For low temperatures ($kT \ll J_0$) and low fields ($g\beta B \ll kT$) the limiting susceptibility is given by

$$\chi = \frac{Ng^2\beta^2}{J_0} \left[\frac{2J_0}{kT} \right] f_1(\alpha), \quad (7)$$

where the function $f_1(\alpha)$ is given by

$$f_1(\alpha) = \int_0^\infty \frac{x^{1-\alpha} e^{-x}}{(1+3e^{-x})^2} dx, \quad (8)$$

with $x = J/kT$. To an accuracy of $\pm 3\%$, f_1 is approximated by

$$f_1(\alpha) = 0.445 \exp(-0.633\alpha). \quad (9)$$

For $[\text{NMP}] [\text{Ni}(\text{mnt})_2]$ the data below 70 K could be fit very satisfactorily into (7) for $\alpha = 0.85$ (figure 6) and for a concentration of random exchanges, $C = 0.05$. Hence it is observed that 5% of the exchanges are distributed randomly with a maximum cut-off at $2J$.

It should be noted from the crystal structure that the dimers are well isolated from each other as is evident from the very different Ni-Ni alternation distances along the a -axis. This would mean that the interdimer interaction (J') is negligible in comparison with J . This was further confirmed as follows: (i) Equation (2) was found to be adequate to interpret the observed data and (ii) the fitting was tried with the expression (4) of Hatfield *et al* (1982) for different values of α , but the best fit was obtained only for $\alpha = 0$.

5.2 Magnetic susceptibility of $[\text{NBu}_4] [\text{Ni}(\text{mnt})_2]$

The magnetic susceptibility was measured on the powder sample of $[\text{NBu}_4] [\text{Ni}(\text{mnt})_2]$ to have an estimate of the exchange coupling constant. The variation of paramagnetic susceptibility with temperature after correcting for temperature independent contributions ($N\alpha + \chi_M^{\text{dia}}$) is shown in figure 8. The susceptibility data could not be fitted satisfactorily into (2) which as such does not take the interdimer interactions into account. Alternatively the data were fitted using (4) by least squares minimization procedures to get $2J = -226 \pm 2 \text{ cm}^{-1}$, $g = 2.061 \pm 0.002$ and $\alpha = 0.045 \pm 0.005$. The agreement is excellent as shown in figure 8. As the $\text{Ni}(\text{mnt})_2$ chains are well separated by the bulky $[\text{NBu}_4]^+$ cations no correction for the interchain interaction was considered significant.

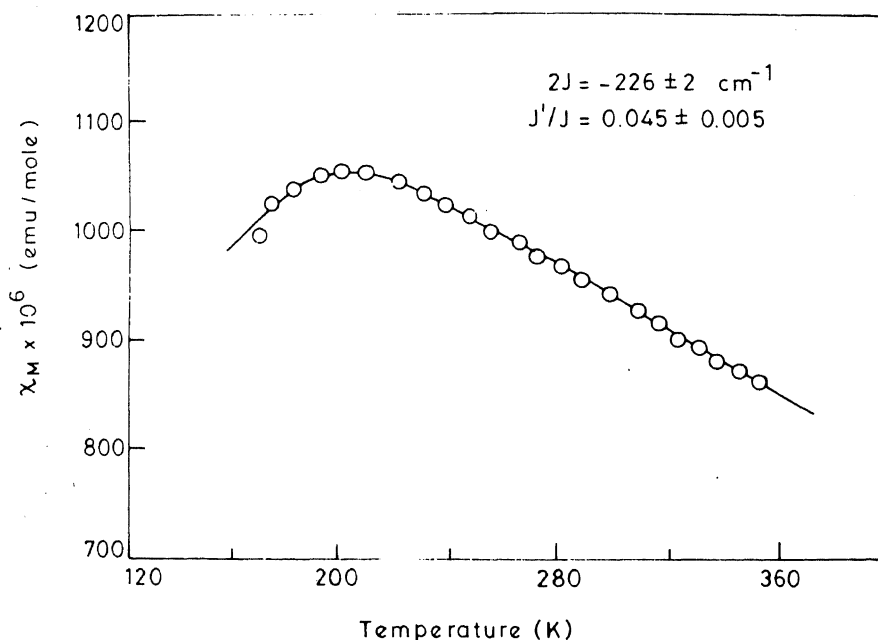


Figure 8. χ vs T for $[\text{NBu}_4] [\text{Ni}(\text{mnt})_2]$. The solid line is the theoretical fit for (4) with $2J = -226 \pm 2 \text{ cm}^{-1}$ and $J'/J = 0.045 \pm 0.005$, while the circles are experimental values.

5.3 Structure-magnetism of dimers

The available magnetic and structural data on $[\text{Ni}(\text{mnt})_2]^-$ dimers may be used to make a few generalizations regarding the strength of exchange coupling and the structure of the dimer. A schematic view of the structure of a typical dimer is shown in figure 9. In all the known $[\text{Ni}(\text{mnt})_2]^-$ dimers the Ni–Ni distance ranges from 4.0 to 4.4 Å. While direct Ni–Ni bonding at this distance is clearly ruled out, the superexchange mechanism involving empty $3d_{xy}$ and $3d_{z^2}$ orbitals of sulphur as proposed by Weiher *et al* (1964) has to be invoked to account for the observed spin-spin coupling. A schematic sketch of the superexchange pathway is presented in figure 10. In this mechanism a delocalization of the odd electron from a nickel $3d_{xy}$ orbital into the empty $3d_{xy}$ orbital of an in-plane bonded sulphur atom occurs which in turn polarises by spin-exchange the weak bond that is formed by the

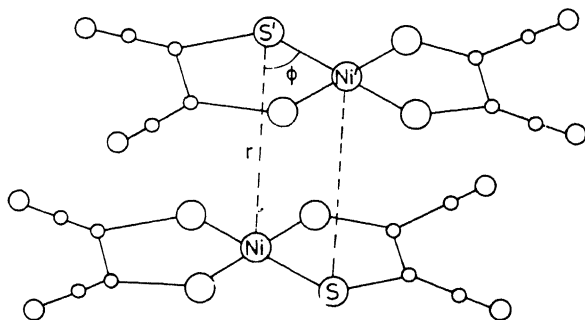


Figure 9. Structure of a typical $[\text{Ni}(\text{mnt})_2]^-$ dimer.

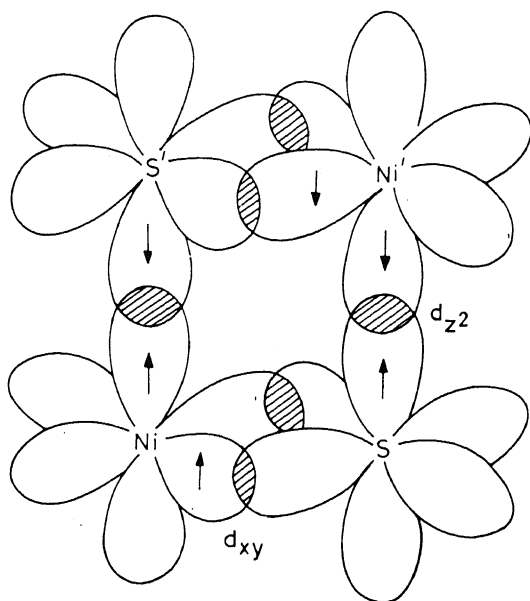


Figure 10. Superexchange pathway for the antiferromagnetic exchange coupling $[\text{Ni}(\text{mnt})_2]^-$ dimers (Weiher *et al* 1964).

interaction of doubly occupied d_{z^2} orbital of Ni' with the empty S-d_{z^2} orbital. Now the spin correlation between the odd electron in $\text{Ni}'\text{-d}_{xy}$ and the polarised electrons of the $\text{Ni}'\text{-S}$ weak bond results in an antiferromagnetic alignment of the two odd electrons. This coupling is further enhanced by the cooperative interaction of the two correlation pathways. Such a pair wise correlation should depend very critically on the nickel-out-of-plane sulphur distance (r) as well as the $\text{Ni-S}'\text{-Ni}$ bridge angle (ϕ). A collection of such parameters along with the known exchange coupling constants is presented in table 1.

The relative disposition of the two $[\text{Ni}(\text{mnt})_2]^-$ units in a dimer as viewed down the normal to the chelate plane is shown in figure 11 for the compounds listed in table 1. A comparison of the overlap in $[\text{NMP}] [\text{Ni}(\text{mnt})_2]$ (figure 4) with those in figure 11 shows that in the former case the overlap is different. In $[\text{NMP}] [\text{Ni}(\text{mnt})_2]$ there are two out-of-plane sulphur atoms which are almost equidistant from the nickel atom and with different bridging angles. The other three systems, $[\text{NBu}_4]^+$, $[\text{NEt}_4]^+$ and $[\text{P}(\text{Ph})_3\text{Me}]^+$ have almost identical disposition with a distinct $\text{Ni-S}'\text{-Ni}'$ overlap.

In the case of hydroxo-bridged Cu-Cu dimers a linear dependence of J on ϕ has been observed (Crowford *et al* 1976; Hatfield 1974; Hodgson 1975) while in the case of chloro as well as sulphur bridged Cu-Cu dimer, J has been shown to depend on ϕ/r (Hatfield *et al* 1980; Hatfield 1983). An inspection of the parameters in table 1 shows that in $[\text{Ni}(\text{mnt})_2]^-$ cases both ϕ and r are important. A plot of $-2J$ versus ϕ/r for the four systems in figure 12 shows a linear variation of J with ϕ/r . The deviation of $[\text{NMP}]^+$ system from the fit is quite reasonable as there are two different superexchange pathways available. However, we need additional data on similar systems to confirm the linear dependence. The exchange coupling constant ($-2J$) or more precisely the singlet-triplet separation is related to ϕ/r as

$$-2J = 106.5 \text{ deg}^{-1} (\phi/r \text{ deg.cm}^{-1}) - 2240 \text{ cm}^{-1}. \quad (10)$$

It must, however, be mentioned that the form and correctness of the above expression is to be tested with data on a few more similar systems and also be justified by theoretical calculations. At present we are carrying out the susceptibility and structural studies on two more dimeric systems namely, $[\text{NPhMe}_3] [\text{Ni}(\text{mnt})_2]$ (Mahadevan *et al* 1983) and [crystal violet] $[\text{Ni}(\text{mnt})_2]$ and we hope to come out with more data to substantiate the above predictions. Also we

Table 1. Structure and magnetic data for $[\text{R}]^+ [\text{Ni}(\text{mnt})_2]^-$ dimers.

$[\text{R}]^+$	Ni-S^a (Å)	$\text{Ni} \dots \text{S}^b$ * (r , Å)	$\text{Ni} \dots \text{Ni}$ (Å)	d^c Å	$\text{Ni}' \dots \text{S-Ni}$ (ϕ , deg)	$-2J$ (cm^{-1})
$[\text{P}(\text{Ph})_3\text{Me}]^+$	2.147	3.591	4.400	3.353	96.7	620 ^d
$[\text{NEt}_4]^+$	2.149	3.515	4.137	3.516	90.5	490 ^d
$[\text{NBu}_4]^+{}^e$	2.147	3.640	4.026	3.541	83.6	226
$[\text{NMP}]^+$	2.142	3.900 (4.096)	4.113	3.581	80.1 (75.4)	241

^a Short in-plane Ni-S bond distance;

^b Long out-of-plane bond distance;

^c Interplanar distance;

^d Weiher *et al* 1964;

^e Isomorphous to the Cu(III) analog (Forrester *et al* 1964).

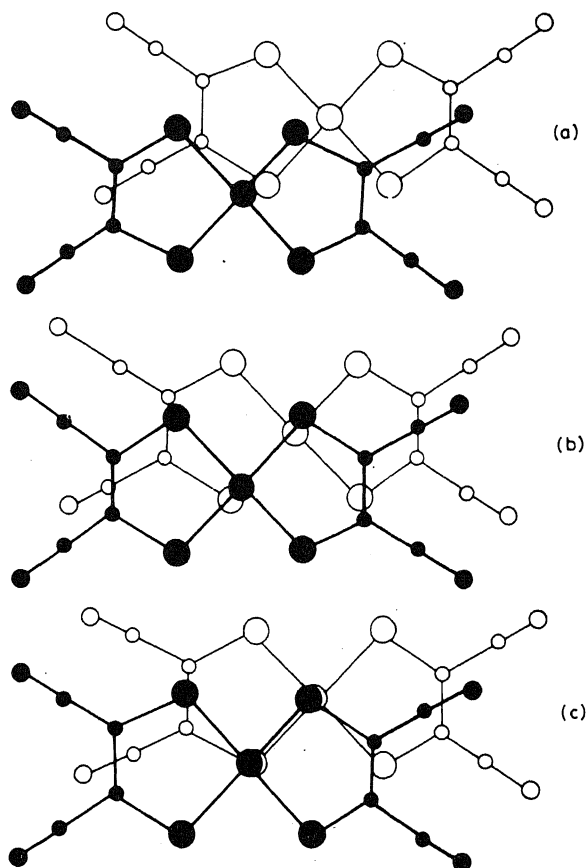


Figure 11. Projection of one of the two $[\text{Ni}(\text{mnt})_2]^-$ ions onto the plane of the other of the dimer (a) $[\text{P}(\text{Ph})_3\text{Me}][\text{Ni}(\text{mnt})_2]$; (b) $[\text{NEt}_4][\text{Ni}(\text{mnt})_2]$; (c) $[\text{NBu}_4][\text{Ni}(\text{mnt})_2]$.

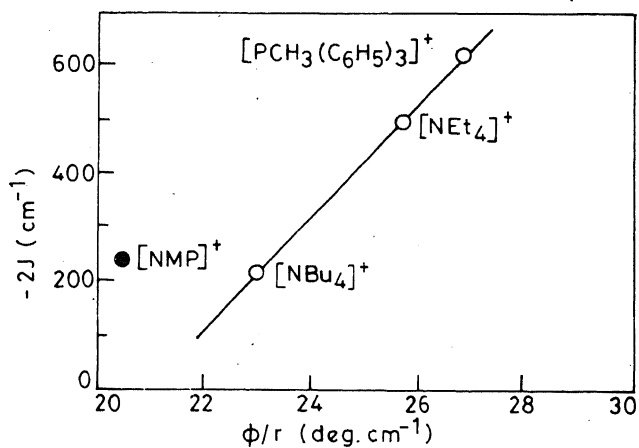


Figure 12. Correspondence between $-2J$ and ϕ/r for $[\text{Ni}(\text{mnt})_2]$ dimers.

are trying to estimate the magnitude of the exchange coupling constant from purely theoretical basis knowing the structure of the dimers.

6. Conclusion

The *bis*(maleonitriledithiolato)nickel(III) complexes show alternation in the metal ion stack and this results in the formation of exchange coupled pairs. The magnetic susceptibility measurements indicate that there is strong demagnetisation due to antiferromagnetic exchange coupling between the ions within the dimer. The exchange coupling constant is very sensitive to the structure of the dimeric unit. The results have been used to obtain a correlation between the structure and magnetism of exchange coupled $[\text{Ni}(\text{mnt})_2]^-$ dimers. A linear dependence of J on ϕ/r has been proposed.

Acknowledgement

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Recent progress in experimental one-dimensional magnetism

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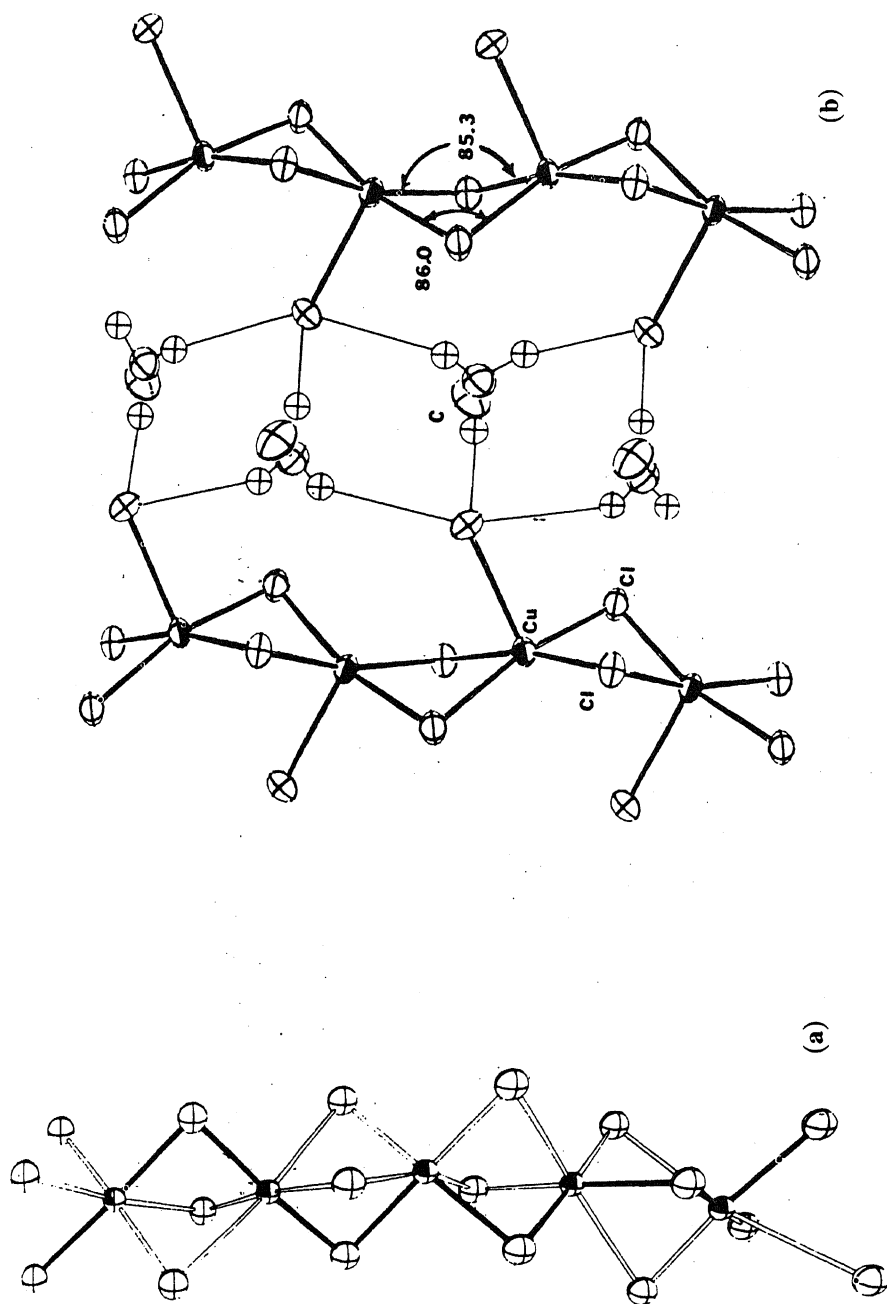
Abstract. New phenomena characteristic of one-dimensional magnetism have been studied in model systems: quantum effects in one-dimensional Heisenberg ferromagnets (1D-HF) with $S = 1/2$ and in one-dimensional Heisenberg antiferromagnets (1D-HAF) with $S = 1$; peculiar anisotropic behaviour of electron spin resonance (ESR) at low frequency and high temperature. The magnetic susceptibility in $(\text{CH}_3)_4\text{NCuCl}_3$ and $(\text{C}_6\text{H}_{11}\text{NH}_3)\text{CuBr}_3$, close to the $S = 1/2$, sD-HF show the expected deviation from the classical behaviour while the recently predicted quantum energy gap for the 1D-HAF is observed in $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NO}_2\text{ClO}_4$. Low frequency ESR in $(\text{CH}_3)_4\text{NMnCl}_3$, the archetype of 1D classical AF, is highly sensitive to the polarization of the oscillating field. In particular, for field direction along the chain axis, the signal is strongly enhanced while it remains at its expected value for perpendicular orientation. This behaviour is related to the axial symmetry of the system.

Keywords. One-dimensional magnetism; Heisenberg ferromagnets; Heisenberg antiferromagnets; quantum energy gap; electron paramagnetic resonance.

1. Introduction

Since the early work of Ising (1925), a lot of theoretical studies have been devoted to one-dimensional (1D) magnetism. In contrast with what happens in three dimensions, exact solutions and accurate approximations have been developed for several 1D magnetic models (Bonner 1985). In the last two decades the interest in 1D magnetism has been strongly renewed with the synthesis of many magnetic compounds which exhibit a quasi-1D magnetic behaviour. Besides the opportunity for checking the numerous theoretical predictions, this opened a new research area in magnetism, owing to the peculiarities of 1D magnetic systems. One of these peculiarities is the absence of a long range magnetic ordered phase at any finite temperature for the ideal 1D system with short range interactions. However, a short range order (SRO) arises as T decreases below $|J|S(S+1)/k$ (where J is the intrachain exchange interaction and S the spin). This SRO is characterized by a correlation length $\xi(T)$ which diverges as T tends to zero. For isotropic interactions described by the Heisenberg-Dirac hamiltonian $\mathcal{H} = -J \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1}$, the high temperature spin dynamics are also very different from that of 3D systems. Since the total spin component $\sum_i \mathbf{S}_i^\alpha$ ($\alpha = x, y, z$) commutes with $\mathcal{H}$, the time correlation functions $\langle S_i^\alpha(0) S_j^\alpha(t) \rangle$ decay slowly as $t^{-1/2}$ at long times. This slow diffusive behaviour partly inhibits the usual exchange narrowing process and leads to drastic

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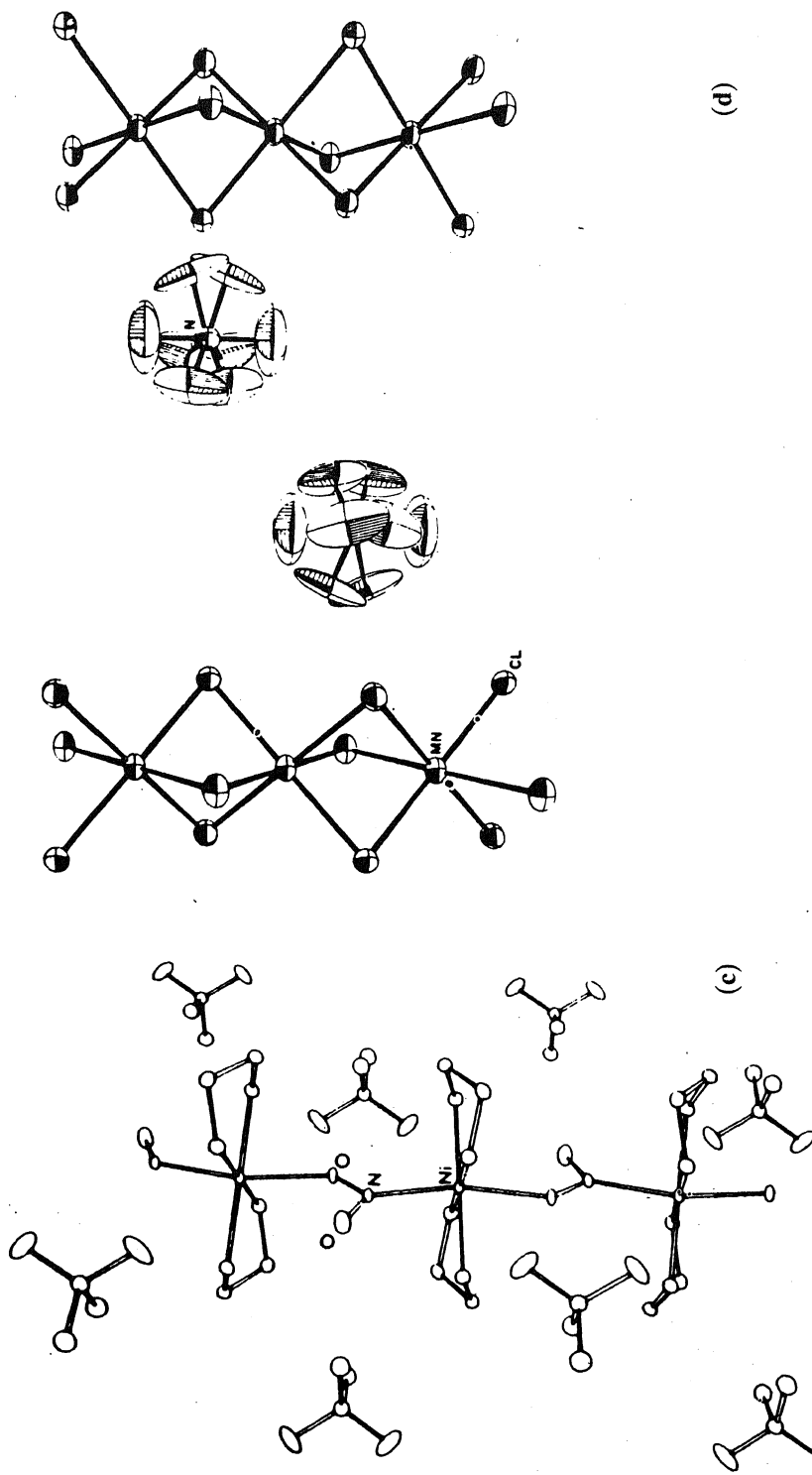


Figure 1. Schematic crystallographic structures of the materials studied: a. Chain structure of TMCuC (Willett *et al* 1983); b. Projection of the crystal structure of CHAC on to the *bc* plane; CHAB is isostructural with CHAC (Willett *et al* 1983); c. Perspective view of NENP; Chains are parallel to *b* axis (Meyer *et al* 1982); d. Crystal structure of TMMC; the MnCl_3 chains are parallel to *c* axis (Willett *et al* 1983).

variations of the EPR line-width and NMR relaxation times with the applied magnetic fields. At low temperatures, where SRO takes place, the spin dynamics is governed by 1D spin waves and in some cases by nonlinear excitations, known as magnetic solitons.

The peculiar behaviour of the static and dynamic magnetic properties at $D = 1$ has been well-evidenced by experiments performed on so-called model systems in which the interchain interactions are much smaller than the intrachain one. The results are reported in several review papers (De Jongh and Miedema 1974; Steiner *et al* 1976; De Jongh 1981; Renard 1985). We restrict there to a few new phenomena not yet reviewed, which are characteristic of 1D magnetism:

- (i) the quantum effects exhibited at low temperature by the one-dimensional Heisenberg antiferromagnet (1D-HAF) with spin $S = 1$ and by the one-dimensional Heisenberg ferromagnet (1D-HF) with spin $S = 1/2$;
- (ii) the *anomalous* behaviour of the ESR lines at low frequencies and high temperatures in the nearly ideal 1D-HAF, $(\text{CH}_3)_4\text{NMnCl}_3$ (TMMC). Figure 1 displays the crystallographic structures of the compounds studied.

2. Quantum effects in 1D-magnetic systems

2.1 Theoretical survey

It is well-established from the renormalization group theory (Wilson 1971) that the value of the spin is not a relevant parameter for the critical behaviour of 3D magnetic systems. Indeed, the values of the critical exponents do not depend on S , as shown by the series expansion calculations as well by the experiments on magnetic compounds (Kadanoff *et al* 1967). Furthermore as T tends to zero, the functional shape of the spontaneous magnetization M_s is also independent of S : $M_s(T) = M_s(0) - aT^{3/2}$ for Heisenberg ferromagnets (HF), $M_s(T) = M_s(0) - bT^2$ for Heisenberg antiferromagnets (HAF). The kinematic interaction between spin waves, which arises from the fact that more $2S + 1$ units of reversed spin cannot be attached to the same atom simultaneously, can be neglected in an expansion in powers of $kT/|J|$ (Dyson 1956; Oguchi 1960). The zero point spin reduction in 3D-HAF is the only quantum effect which deserves to be mentioned. The relative spin reduction is roughly given by $\delta S/S \approx 1/zS$ where z is the number of neighbours interacting with a given spin. The predicted spin reduction is generally small in true 3D system. It is substantially larger in quasi 2D-antiferromagnets in which it has been measured by neutron diffraction and nuclear magnetic resonance (Walstedt *et al* 1970; De Wijn *et al* 1973).

In contrast with 3D systems, drastic quantum effects are predicted for 1D systems. Let us consider, at first, the case of one-dimensional ferromagnets (1D-F). The correlation functions of the classical 1D Heisenberg system have been determined by Fisher (1964). As T tends to zero, the correlation length diverges as T^{-1} and consequently the magnetic susceptibility of the 1D-HF proportional to T^{-1} . χ diverges as T^{-2} . The same T^{-2} susceptibility behaviour is also obtained for the classical 1D-XY ferromagnet. The magnetic susceptibility of the $S = 1/2$, 1D-HF cannot be obtained exactly but approximate treatments have been developed by different authors (Bonner and Fisher 1964; Baker *et al* 1964; Lyklema

1982). They indicate a power law divergence $\chi(T) = AT^{-\gamma}$ as $T \rightarrow 0$, with an exponent γ lower than the classical value $\gamma_{cl} = 2$. The theoretical estimates presently available range between 1.67 (Baker *et al* 1964) and 1.8 (Bonner and Fischer 1964). The recent synthesis of a few $S = 1/2$, 1D-F with small magnetic anisotropy allows the testing of the predicted quantum reduction of the exponent γ . First experimental results will be presented in §2.2.

A more striking quantum effect at $D = 1$ concerns the structure of the lowest energy states of the 1D-HAF. It has been recently conjectured by Haldane (1983) that this structure is completely different for integer and noninteger spin values. The $S = 1/2$, 1D-HAF has been theoretically investigated by des Cloizeaux and Pearson (dCP) (1962). It exhibits an ordered ground state and a quasi-continuum of excited states without gap from the ground state. The magnetic excitations of lowest energy are $E = \pi/2 |J| |\sin q|$ and appear to be very similar to the classical 1D-HAF which has also a sine dispersion relation: $E = 2 |J| S |\sin q|$. The neutron diffraction experiments performed in the 1D-HAF TMMC, with $S = 5/2$ (Hutchings *et al* 1978) and $\text{CuCl}_2 \cdot 2\text{N}(\text{C}_5\text{D}_5)$, (CuPC) with $S = 1/2$ (Heilmann *et al* 1978) support the theoretical predictions. Subtle quantum effects are revealed from the neutron scans in CuPC, firstly near the zone boundary $q = 1$, where additional excitations of higher energy than the dCP ones are observed, and secondly in the excitation spectrum in an applied magnetic field. Owing to the similarity between the $S = 1/2$ - and the classical 1D-HAF, it was thought until recently that the intermediate cases, such as $S = 1$, were of little interest. The interest in the 1D-HAF with integer spin values has been renewed by Haldane (1983) who predicted, for these systems, an energy gap between the singlet ground state and the first excited states. Botet *et al* (BJK) (1983) investigated in detail the properties of the $S = 1$, 1D Heisenberg-Ising antiferromagnet described by the following Hamiltonian

$$\mathcal{H} = \sum_i [-J(S_i^x S_{i+1}^x + S_i^y S_{i+1}^y + \lambda S_i^z S_{i+1}^z) + D(S_i^z)^2], \quad (1)$$

where J represents the intrachain exchange interaction, $1 - \lambda$ the exchange anisotropy and D the single-ion anisotropy. For a certain range of λ and D values, there is a novel phase with an unordered singlet ground state and an energy gap to the excited states continuum. The gap exhibits a nontrivial variation with the magnetic anisotropy which is sketched in figure 2. Haldane's predictions and the results of BJK were confirmed by finite size calculations up to $N = 14$ for $S = 1$ (Parkinson and Bonner 1985) and by a Monte Carlo calculation up to $N = 32$ (Nightingale and Blöte 1986). They provide a good estimation for the energy gap of the $S = 1$, 1D-HAF: $E_G \approx 0.4 |J|$. These predictions for the 1D-HAF with $S = 1$, are compared to the experiments on the new model system $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)\text{NO}_2\text{ClO}_4$ in §2.3.

2.2 Low temperature magnetic susceptibility of two $S = 1/2$, 1D ferromagnets: TMCuC and CHAB

Among the series of $S = 1/2$, 1D ferromagnets recently discovered (Willett *et al* 1983; Willett 1985), $(\text{CH}_3)_4\text{NCuCl}_3$ (TMCuC) and $(\text{C}_6\text{H}_{11}\text{NH}_3)\text{CuBr}_3$ (CHAB) are especially attractive because of their low 3D magnetic ordering temperature, $T_N = 1.24$ K for TMCuC (Dupas *et al* 1982) and $T_N = 1.5$ K for CHAB (Kopinga

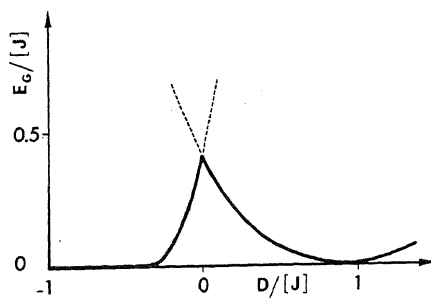


Figure 2. Variation of the energy gap between the ground state and the first excited state of the $S = 1$, $1D$ -AF, with the single ion anisotropy parameter D ($\lambda = 0$). $D = 0$ corresponds to the pure Heisenberg case. $D < 0$ to XY type anisotropy and $D > 0$ to Ising type anisotropy (after Botet *et al* 1983).

et al 1982), compared to the intrachain interaction of about 100 K (see figure 1a, b). The magnetic anisotropy of TMCuC is not known since single crystals of this compound were not available. It is likely to be small because of the octahedral symmetry of the local environment of the Cu^{2+} ion. For CHAB, the ferromagnetic resonance experiments (Phaff *et al* 1984) show a planar anisotropy of 5% of the isotropic exchange interaction $J/k = 110$ K (Kopinga *et al* 1982).

The magnetic susceptibility of powdered TMCuC at low temperature ($kT/J < 0.3$) is shown in figure 3. The experimental data are fairly consistent with the series expansion calculations of Baker *et al* (1964) for the $S = 1/2$, $1D$ -HF for $J/k = 88$ K. They can be fitted by the power law $T^{-1.58}$ between 2.3 K and 20 K. The deviations from this power law which occur below 2.3 K are certainly related to the $3D$ interactions which induce antiferromagnetic long range order at $T_N = 1.24$ K. From these susceptibility data, it appears that TMCuC behaves as a nearly ideal $S = 1/2$, $1D$ -HF and exhibits the predicted quantum reduction of the susceptibility critical exponent as T tends to zero. The susceptibility of a small monocrystal of CHAB, grown by Dr C Landee, has been measured with a low field SQUID magnetometer (Beauvillain *et al* 1985), along the crystal axes c (easy plane) and a (hard axis). The experimental data in figure 4, show the drastic effect of magnetic anisotropy, at temperatures below 30 K, the susceptibility along the hard axis being much smaller than the one along the easy axis, except at the vicinity of the $3D$ ordering temperature where the interchain interactions become predominant. For the easy direction c , the experimental data cannot be described in a wide temperature range by a power law with a unique value of the exponent; in fact, the effective exponent between 20 K and 3 K, varies from 1.75 to about 2. The quantum reduction from the classical exponent 2 is thus less important in CHAB than in TMCuC. This could be related to the planar anisotropy which has been taken into account in the recent quantum Monte Carlo study of Satija *et al* (1985). These authors calculated the susceptibility of CHAB along the easy plane between 5 and 20 K. Their results which are consistent with a $T^{-1.75}$ law, are in good agreement with the experimental data above 8 K; precise calculations at lower kT/J values are clearly needed for an extensive comparison with the experiment.

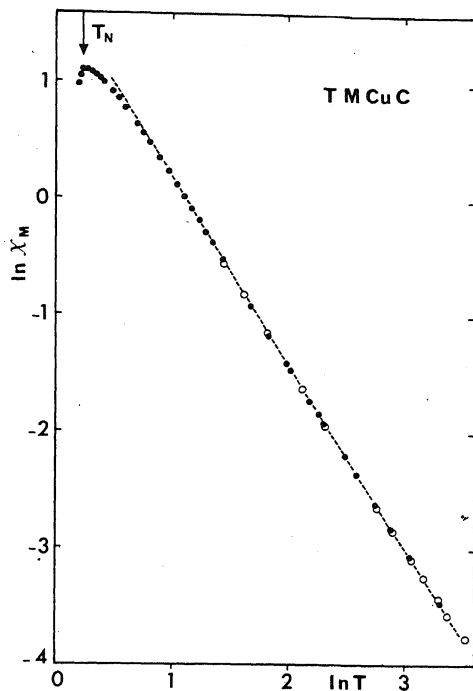


Figure 3. Molar susceptibility of TMCuC powder in cgs emu as a function of temperature, on a double neperian logarithmic scale: (●) experimental data; (○) series expansion of Baker *et al* (1964) for $J/k = 88$ K. The dotted line represents the power law $T^{-1.58}$.

2.3 Experimental study of NENP a quasi-1D Heisenberg antiferromagnet with $S = 1$.

It is surprising that the quantum gap in the quasi-1D-HAF with integer spin value was not observed until very recently. Indeed, the existence of an energy gap E_G between the singlet ground state and the first excited states would produce drastic effects on the magnetic properties. At temperatures below E_G/k , the magnetic susceptibility $\chi(T)$ would exhibit a fast decrease with T and tends to a value, $\chi(0)$, much smaller than the maximum one, $\chi_{\max}$ at $T \approx |J|/k$, for all magnetic field orientations. In addition, since the correlation length does not diverge as $T \rightarrow 0$, the quasi 1D-HAF with a gap cannot develop 3D magnetic long range order (LRO) if the interchain exchange interaction J' is sufficiently small.

In fact, until recently, the better 1D-HAF with $S = 1$ was CsNiCl_3 for which $|J|/k = 26$ K and $|J'/J| \approx 10^{-2}$. This compound which is far from ideal, does not exhibit the expected behaviour for a gap system, either in the thermal variation of the susceptibility or in the absence of LRO ($T_N = 4.85$ K). Nevertheless, indirect indications for a quantum gap in CsNiCl_3 have been recently reported from inelastic neutron scattering experiments (Buyers *et al* 1986).

A possible way to approach the ideal $S = 1$, 1D-HAF is to increase $|J|$ and the interchain distance. This is realized in $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NO}_2\text{ClO}_4$, hereafter abbreviated as NENP (figure 1c). In the orthorhombic crystal of NENP, the nickel ions are covalently linked by nitrito groups along the *b* crystal axis. This insures a large

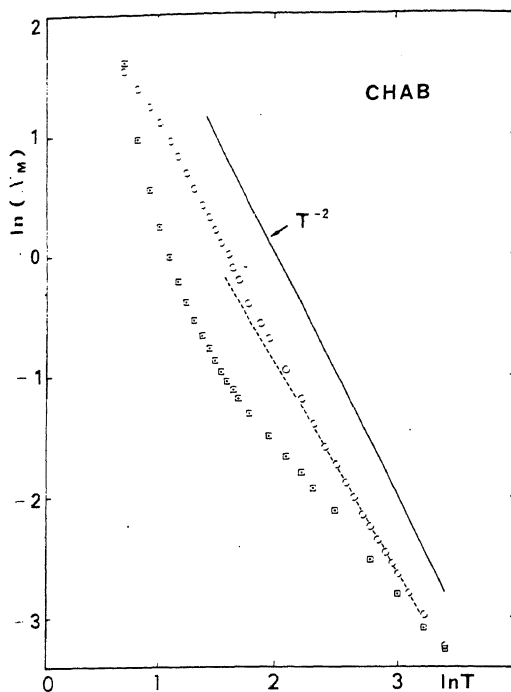


Figure 4. Molar susceptibility of a CHAB single crystal in egs emu as a function of temperature, on a double neperian logarithmic scale: (○) experimental data for field along *c*; (□) experimental data for field along *a*; the dotted line represents the theoretical estimates for $S = 1/2$, 1D-XY ferromagnet (Satija *et al* 1985); the full line represents the classical law T^{-2} .

antiferromagnetic exchange interaction $J/k = 50$ K, while the planar anisotropy determined from high temperature susceptibility is small, $D/k \approx 1$ K (Meyer *et al* 1982). The magnetic chains are well separated from each other by ClO_4^- anions, which leads to a small value of the interchain interaction $|J'/J| \approx 4 \times 10^{-4}$ (Renard *et al* 1987).

The magnetic susceptibilities of a single crystal of NENP, along the three orthogonal crystal axes *a*, *b* and *c* have been measured with a SQUID magnetometer (Beauvillain *et al* 1985) down to 1.7 K (figure 5). For all field orientations, the susceptibility exhibits a rounded maximum at about 60 K, in agreement with the previous measurements and falls down abruptly as the temperature is lowered below 15 K. The ratio $\chi(0)/\chi_{\max}$ ranges between 3×10^{-2} and 10^{-1} for the various field orientations. These values are much smaller than the theoretical ones for a gapless 1D-HAF [$\chi(0)/\chi_{\max} = 0.69$ for $S = 1/2$ and 0.83 for $S = \infty$]. The behaviour of the susceptibility of NENP clearly indicates an energy gap E_G between a singlet ground state and the excited states. By fitting the low temperature decay of $\chi(T)$ with an exponential law, $\exp(-E_G/kT)$, a rough estimate of E_G/k of about 14 K is obtained. However the lack of theoretical data relative to the temperature dependence of $\chi(T)$ for the $S = 1$, 1D-HAF forbids a quantitative analysis.

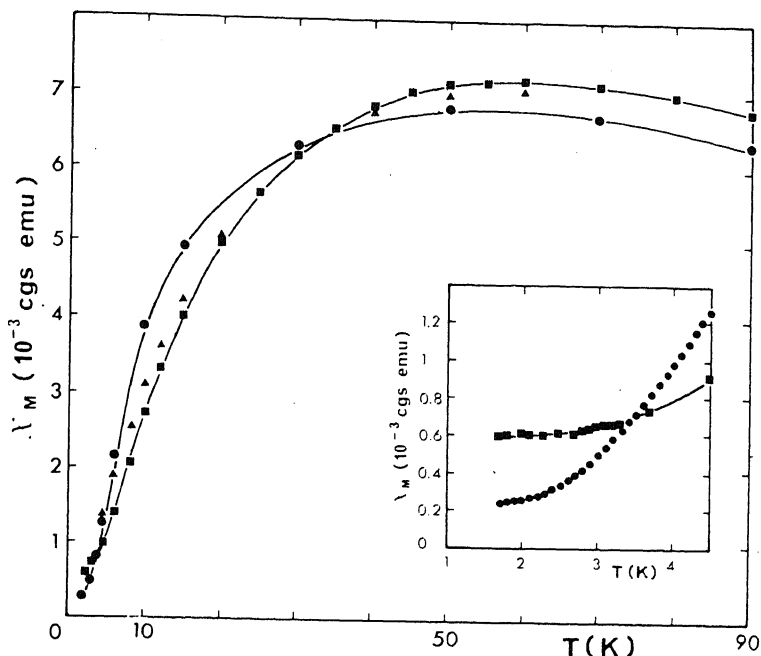


Figure 5. Molar susceptibility of the quasi-1D-HAF with $S = 1$, NENP, along the three crystal axes *a* (■), *b* (●) and *c* (▲) as a function of temperature. The solid lines are guides for the eye. Notice the abrupt decrease of the susceptibilities below 15 K due to the quantum energy gap.

A second clear manifestation of the energy gap in NENP is the absence of 3D-LRO. For a gapless Heisenberg model with $J/k = 50$ K and $|J'/J| = 4 \times 10^{-4}$, the Néel temperature approximated as $T_N \approx 2S^2(J, J')^{1/2}/k$, is equal to about 2.5 K. There is no experimental evidence for such a transition in the susceptibility curves of figure 5. In addition, the proton magnetic resonance spectra of a single crystal of NENP were recorded at 77 K and between 1.2 and 4.2 K. The spectra which show negligible temperature dependence of the resonance fields are characteristic of a disordered magnetic phase.

From detailed inelastic neutron scattering experiments, the excitation spectrum of NENP was determined for different scattering vectors (Renard *et al* 1987). These measurements show two energy gaps corresponding to fluctuations of the spin components parallel and perpendicular to the chain axis, at respective values $E_G/|J| = 0.26$ and $E_G/|J| = 0.58$. The existence of two gaps, instead of one for the pure $S = 1$, 1D-HAF is due to the magnetic anisotropy ($D \neq 0$) and is consistent with the predictions of BJK (figure 2). One can reasonably assume that the average of the two gap values, $E_G/|J| = 0.4$ is a good estimate of the unique gap of the 1D-HAF. Indeed a good agreement is found with the theoretical predictions $E_G/|J| = 0.38$ (Parkinson and Bowner 1985) and 0.41 (Nightingale and Blöte 1986).

3. Low frequency electron spin resonance in 1D magnetic systems

3.1 High temperature 1D spin dynamics and ESR

In concentrated paramagnetic exchange coupled systems the ESR lines are Lorentzian in shape and relatively narrow, considering the dipolar interaction between spins. This "exchange narrowing" (Pake 1962) is related to the exchange interaction J between the spins, and can be described as a mechanism which flips the spins at a $|J|/\hbar$ rate and randomizes broadening processes.

More precisely, it can be shown, within linear response theory (Pake 1962), that the ESR absorption from a field $\mathbf{B}_1 \cos \omega t$ linearly polarized along the x -axis is proportional to the Fourier transform of the magnetization correlation function

$$G_x(t) = \langle S_x(t) S_x(0) \rangle,$$

$$A_x(\omega) \propto \int_{-\infty}^{+\infty} \langle S_x(t) S_x(0) \rangle \exp(-i\omega t) dt, \quad (2)$$

the bracket denoting a statistical average, and the time dependence of the total spin component S_x being due to the spin Hamiltonian of the system (essentially exchange, Zeeman, and dipolar coupling terms).

$G_x(t)$ itself is related to local time-spin correlation functions which, in 3D systems, decrease to zero in a very short time $1/J$ so that $G_x(t)$ falls down exponentially with a time constant T_2 . A Lorentzian line with half-width (in angular units) $1/T_2 \sim (\omega_d/\hbar)$ (ω_d/J) results, ω_d being a dipolar coupling factor.

Significant deviations from this behaviour are observed in quasi one-dimensional systems such as TMMC. They have been thoroughly studied for the last fifteen years, essentially in the microwave frequency range (Dietz *et al* 1971; Reiter and Boucher 1975; Cheung *et al* 1978; Natsuma *et al* 1980; Siegel *et al* 1982).

The ESR 1D spectrum is highly anisotropic and two orientations are of special interest. In the following, θ is the angle between the axis of the chain (c axis of the crystal) and the static field $\mathbf{B}_0$. When the static field $\mathbf{B}_0$ points along the chain axis ($\theta = 0^\circ$) a non-Lorentzian broad line is observed while at the magic angle orientation ($\theta = 55^\circ$) the line is narrow and Lorentzian: in this latter case the secular part of the dipolar interaction between spins is cancelled. These features [and other ones: strong sensitivity to impurities (Richards 1974), side band effects (Lagendijk 1978)...] are well-explained by the long-lived local correlation functions. The Heisenberg coupling flips the spins without changing the total magnetization of a chain and the local correlation functions are expected to have 1D diffusive long-time behaviour $t^{-1/2}$. Owing to this very slow decay, the description of the absorption line profile is much more complicated than in 3D paramagnets because the damping factor now varies as the static field is swept through the absorption line. It gives rise to shape alteration and a half-width $\sim (\omega_d/J)^{1/3} \cdot \omega_d/\hbar$. At magic angle, however, the non secular dipolar terms are quickly modulated at Larmor frequency and the line remains Lorentzian.

3.2 Low frequency ESR experiments in $(\text{CH}_3)_4\text{N Mn Cl}_3$ (TMMC)

A recent investigation of the TMMC spectrum at very low frequencies (between 2 and 225 MHz) reveals new interesting peculiarities (Clement *et al* 1984). In

general, measuring broad lines at low frequency is not an easy matter: the line amplitude varies as ω^2 , the square of the angular frequency. This power dependence results from the induction law and from the Boltzmann factor. The situation may even be worse since the lines usually broaden when lowering the frequency: this phenomenon is known as the "10/3 effect" (Pake 1962). In the present study we meet three favourable conditions:

- (i) we use large TMMC single crystals (with weighs between 2 and 5.5 g);
- (ii) the apparatus sensitivity is such that synchronous detection is unnecessary, and direct interpretation of the results is possible;
- (iii) we choose a case study (TMMC) where the symmetry of exchange and dipolar interactions permits large effects, as discussed below.

The field orientation of interest is neither the chain direction, nor the magic angle one, but the one when the field is perpendicular to the chain axis ($\theta = 90^\circ$). In this case, a narrowing of the line is observed when the frequency is lowered, i.e. a phenomenon opposite to the one expected from the "10/3 effect". Moreover, the line amplitude is strongly dependent on the orientation of the oscillating field $\mathbf{B}_1$, defined by the angle $\varphi = (\mathbf{B}_1, \mathbf{c})$ (see figure 6). Relative absorption line amplitudes are measured using free radical DPPH as a standard. In the following, we put aside the ω^2 dependence, since it is common to all lines. When lowering the frequency, i) the resonance amplitude is enhanced when the oscillating field $\mathbf{B}_1$ is parallel to the chain axis $\mathbf{c}$; the enhancement factor is about 4 between 225 and 25 MHz. ii) the resonance amplitude remains constant when $\mathbf{B}_1 \perp \mathbf{c}$ ($\varphi = 90^\circ$).

These anomalous features can be explained by a simple model, where TMMC is considered as a set of non interacting spin chains, where the spins are coupled only by intrachain exchange H_{ex} and dipolar H_D interactions.

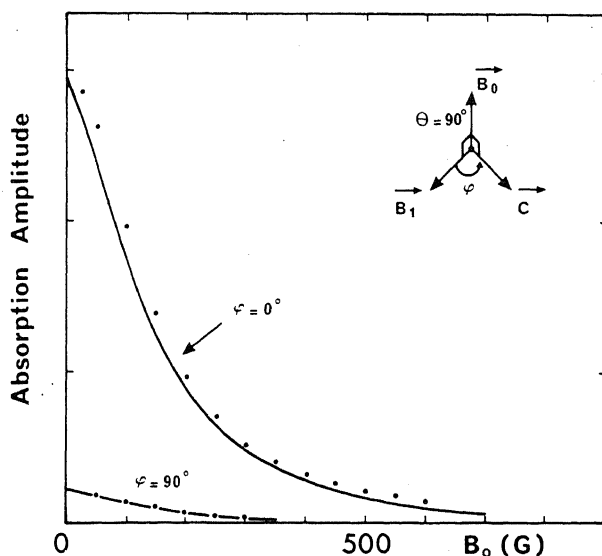


Figure 6. ESR spectrum of TMMC at the frequency $\nu = 25$ MHz for two orientations of the r.f. oscillating field: parallel ($\varphi = 0^\circ$) and perpendicular ($\varphi = 90^\circ$) to the chain axis $\mathbf{c}$. For both cases the static field is perpendicular to $\mathbf{c}$. The solid lines represent the experimental data and circles the theoretical predictions.

In this frame, the S_x total spin component along the chain axis $\mathbf{c}$, supposed to be parallel to the x -direction, is a constant of motion (it commutes with H_{ex} and H_D), while S_y suffers a damping $1/T_2$. If we apply the oscillating field B_1 in the chain direction, in the limit $\omega \rightarrow 0$ the line profile is a delta function.

Let us apply the static field $\mathbf{B}_0$ along the z -direction. The S_x motion is coupled to the S_y motion through the Zeeman interaction. At high frequencies, the modulation at Larmor frequency $\omega_z = -\gamma B_0$, where γ is the gyromagnetic ratio, is so fast that anisotropy effects are very small: we recover the usual line profile. At "low" frequencies ($\omega \lesssim 1/T_2$) S_x suffers a damping which is a function of B_0 and T_2 : the line is characterized by the enhancement of amplitude, the shift in position and its width narrowing.

If the oscillating field $\mathbf{B}_1$ is applied along the y -direction, the absorption line is related to the motion of S_y : no line amplitude enhancement is expected in this case.

In fact chains of spins are weakly coupled and a resulting damping $1/T_2' (\ll 1/T_2)$ occurs. The spectrum may then be accurately described by the following spin motion equations [with (2)], which are Bloch modified equations:

$$\begin{aligned}\dot{S}_x &= \omega_z \cdot S_y - S_x/T_2', \\ \dot{S}_y &= -\omega_z \cdot S_x - S_y/T_2.\end{aligned}\quad (3)$$

For $\omega \ll 1/T_2$ the main results are the following. At $\varphi = 0^\circ$ ($\mathbf{B}_1 \parallel \mathbf{c}$), interchain interactions give rise to zero field absorption, and the signal is

$$A_x(\omega_z = 0) = a \cdot T_2'^{-1}/(\omega^2 + T_2'^{-2}), \quad (4)$$

where a is a constant.

When $\omega < 1/T_2'$, the resonance field is zero. In other cases, the resonance is given by:

$$\omega_z^2 = (\omega - 1/T_2')/T_2, \quad (5)$$

and the resonance signal presents the remarkable property to be almost independent of the damping values:

$$A_x(\text{res}) \simeq a/2\omega. \quad (6)$$

This enhancement at low frequencies is inhibited by interchain interactions when $\omega < 1/T_2'$. This is why the experimental resonance amplitude is enhanced four times and not nine when lowering the frequency from 225 MHz to 25 MHz.

At $\varphi = 90^\circ$ there is no shift and the resonance signal A_y is equal to aT_2 .

From (4) and (6), it is easy to derive the interchain damping $1/T_2' \simeq 6 \times 10^8 \text{ rad s}^{-1}$, and from (5), $1/T_2' \simeq 9.5 \times 10^9 \text{ rad s}^{-1}$. Agreement with experiment appears fairly good (figures 6 and 7).

However, $1/T_2'$, and to a lesser extent $1/T_2$, are slowly decreasing functions of the field B_0 . This field dependence can be directly observed at the "relaxation configuration" (Lagendijk and Schoemaker 1977), when the oscillating field $\mathbf{B}_1$ is parallel to the static one $\mathbf{B}_0$, along the z -axis. In this case, one measures the longitudinal relaxation of the magnetization towards its equilibrium value which is along the z -axis.

This relaxation occurs with a time constant T_1 .

The absorption signal is then

$$A_z = a \cdot T_1^{-1}/(\omega^2 + T_1^{-2}). \quad (7)$$

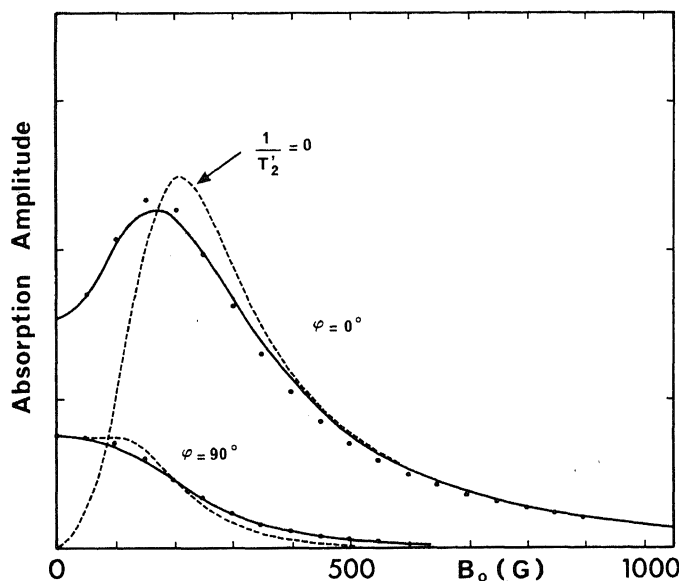


Figure 7. ESR spectrum of TMMC at $\nu = 225$ MHz. The experimental conditions are the same as in figure 6. Solid lines: experiment; circles: theory with $1/T_2' = 0.59 \times 10^9$ rad s $^{-1}$; dashed lines: theory with $1/T_2' = 0$.

Measurements of A_z versus B_0 are shown in figure 8 for two orientations θ of the chain axis c with respect to Oz . Amplitude values are unscaled because zero absorption cannot be attained.

T_1 varies with the chain orientation θ . Longitudinal relaxation is produced mainly by the nonsecular terms of the intrachain dipolar interaction (Bourdel *et al* 1981). But when $\theta = 0^\circ$ these terms cancel and the relaxation is caused by interchain interactions: T_1 coincides with T_2' at zero field. At the operating frequency (225 MHz), $A_z \approx a/\omega^2 T_1$ shows a field dependence somewhat like $1/T_2'$. If the chain axis is perpendicular to the field ($\theta = 90^\circ$) it turns out that $T_1 = T_2$ at zero field, a value $\gg \omega$. Thus $A_z \approx aT_1$, exhibiting an increase with the field similar to the T_2 dependence.

A microscopic theory (Bize 1987) explains satisfactorily the experimental data for all field orientations and frequencies. This theory is in perfect agreement with the simple model based on modified Bloch equations. So far the same damping constants were used in the Bloch equation (3) though interactions are anisotropic in crystalline solids. This approximation is indeed valid at high frequencies ($\omega \gg 1/T_2$) where spin components suffer a mean damping $(1/T_2 + 1/T_2')/2$, $1/T_2'$ in the oscillating field direction B_1 and $1/T_2$ in the direction perpendicular to both fields B_1 and B_0 . But interesting information about local interactions may be obtained from low frequency experiments by varying the oscillating field polarization. To be fair, we must point out that such important effects are observed because TMMC represents an extreme case where the dominant interactions are the exchange ones with spherical symmetry and the intrachain dipolar ones with axial symmetry. This results in extremely small spin damping in the chain direction, hence the magnitude of the observed effects.

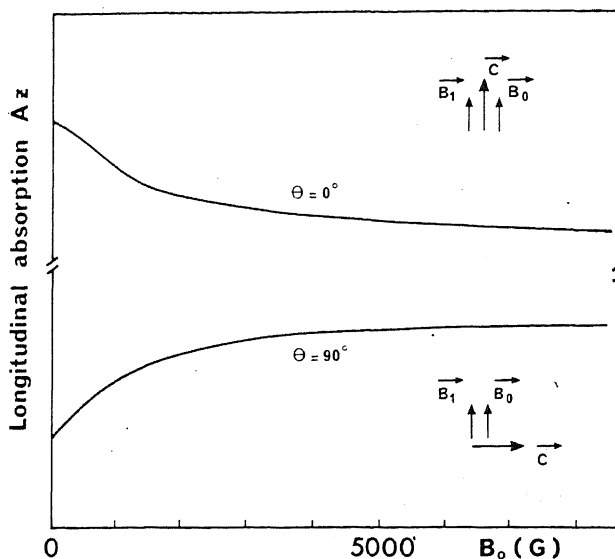


Figure 8. ESR absorption in the "relaxation configuration" i.e. oscillating and static fields parallel to each other. The fields are parallel ($\theta = 0^\circ$) or perpendicular ($\theta = 90^\circ$) to the chain axis. The signals are unscaled.

4. Conclusion

The experimental investigations reported in the preceding sections show how one-dimensional magnetism remains a rich research field in condensed matter. The study of quantum effects in $S = 1/2$, 1D-materials is yet in rapid development. Indeed, magnetic solitons have been recently observed in the ferromagnetic chains of CHAB (Kopinga *et al* 1984) at low temperature. On the other hand, the study of the $S = 1$, 1D antiferromagnets is just at the beginning. It promises interesting developments which include the phase diagram in an applied magnetic field, the low temperature spin dynamics, the direct measurement of the correlation length versus temperature and the effect of magnetic anisotropy on quantum gaps.

The high temperature spin dynamics also remains interesting as shown by the peculiar behaviour of the low frequency ESR. This is a novel method for the direct determination of the interchain exchange interaction, which should be applied to many other 1D compounds than the model system TMMC.

Therefore, new progress in 1-D physics demands endeavours in two directions: (i) development of new instruments and techniques: sensitive magnetometers, versatile ESR spectrometers (low frequency and variable oscillating field direction, Clement *et al* 1984) and low temperature measurements. Instrumental work is underway to make such equipments easily available to the scientific community (Willett 1985);

(ii) synthesis of new compounds with predictable properties, within the chains and between them: this is a challenge for chemists and crystallographers;

1D-F are rare. To obtain new species, the synthesis of bimetallic (A, B) compounds, with orthogonal magnetic orbitals ($A = d^1$; $B = d^9$ for example) is a possible answer.

The study of quantum gaps necessitates new $S = 1$, or 2, 1D-AF with smaller J intrachain exchange interaction, with single ion anisotropy of various kinds, Ising and XY, variable D/J and better J'/J ratio (Ribas *et al* 1987).

New quantum effects might be evidenced in the bimetallic ferrimagnetic chains, with different spins, recently synthesized (Drillon *et al* 1983; Gleizes and Verdaguer 1984; Verdaguer *et al* 1984; Pei *et al* 1987), which deserve to be explored.

Finally, interchain interactions have to be carefully controlled: whether to obtain better 1D materials with bulky insulating groups, or to build at will 2D or 3D networks with expected properties, from ferro or ferrimagnetic 1D linked by well-conceived connections.

We are working along these lines (Pei *et al* 1987)

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Magnetic properties of $A_2Cu_nX_{2n+2}^-$ systems

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Abstract. The magnetic behavior of planar bibridged copper(II) halide dimers, trimers, and tetramers are summarized. The planar oligomers exhibit antiferromagnetic coupling. Dimeric $Cu_2X_6^{2-}$ ions can undergo one of two types of distortions: a tetrahedral twist distortion and a bifold, or sedita, distortion. Both distortions cause the exchange interaction to become ferromagnetic. Trimeric species have a $S = \frac{1}{2}$ ground state. Evidence for non-Boltzman depopulation of the excited quartet state is observed and is tentatively assumed to arise from frustrated intertrimer interactions. Comparison of the $X = Cl$ and $X = Br$ salts show that the antiferromagnetic contribution to the exchange coupling is approximately twice as large for the bromide salts as for the chloride salts. It is also seen that the coupling becomes more antiferromagnetic as the length of the oligomer increases.

Keywords. Copper(II) halide oligomers; magneto-structural correlations.

1. Introduction

Copper(II) halide salts have provided a particularly fruitful field for studying magneto-structural correlations. The flexibility of the copper(II) coordination sphere, coupled with the non-stereospecificity and bridging ability of halide ions, has provided a wide plethora of structures which can be explored (Smith 1976). The d^9 electronic structure of the Cu(II) ion leads to the occupancy of a single magnetic orbital on each metal site and a nearly isotropic (Heisenberg) magnetic exchange coupling. This makes both the analysis of the magnetic data and the theoretical interpretation of the magneto-structural correlations particularly straightforward. It has been shown by Hay *et al* (1978) that the exchange energy, $2J$, for the interaction of two spin $\frac{1}{2}$ ions, can be expressed by the combination of two terms,

$$2J = 2K_{ab} - 2(\epsilon_1 - \epsilon_2)^2/(J_{aa} - J_{bb}) = 2J_F - 2J_{AF}, \quad (1)$$

where the exchange and coulomb integrals, $K_{ab} > 0$, $J_{aa} > J_{bb}$, are slowly varying functions of the molecular parameters while ϵ_1 and ϵ_2 are the energies of the molecular orbitals formed from the magnetic orbitals on the two metal ions. The first term gives a ferromagnetic (FM) contribution; the second an antiferromagnetic (AFM) contribution. Semiempirical techniques (Hay *et al* 1978; Bencini and Gatteschi 1978) have been used to calculate ϵ_1 and ϵ_2 as a function of various molecular parameters. Hence, it is possible to predict qualitatively the effect that a particular change in molecular geometry will have on the strength of the exchange

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coupling. This assumption that K_{ab} can be regarded as independent of geometry has been challenged (Kahn and Charlot 1980).

Experimentally, the foundation of magneto-structural correlation in dimeric systems is based on the results found in copper(II) hydroxide complexes (Hatfield 1985). Considering a planar $\text{Cu}_2\text{X}_2\text{L}_4$ system, it has been demonstrated experimentally that the exchange coupling changes linearly with J with the coupling being FM for angles less than 97.5° , where ϕ is the Cu-L-Cu bridging angle (Hatfield 1985). Calculations (Hay *et al* 1978; Bencini and Gatteschi 1980) show that $\epsilon_1 - \epsilon_2$ varies strongly with angle, with $\epsilon_1 - \epsilon_2 = 0$ at an angle near 90° .

The concept of orthogonality leading to FM interactions shows up more explicitly in the formulation of Kahn and Briat (1976). The exchange constant is written as

$$J = J_F + J_{AF}, \quad (2)$$

where

$$J_F = 2 m^2 \sum J_{\mu\nu}, \quad (2a)$$

and

$$J_{AF} = 2 m^2 \sum \Delta_\mu S_{\mu\mu}. \quad (2b)$$

with $\Delta_\mu = \epsilon_1 - \epsilon_2$ and $S_{\mu\mu}$ is the overlap integral of the two equivalent magnetic orbitals on the two metal atoms. Thus, in this formalism, the AFM contribution clearly disappears when the orbitals are orthogonal.

In this paper, we will discuss the magnetic behavior of symmetrically bibridged $\text{Cu}_n\text{X}_{2n+2}^{2-}$ anions ($\text{X} = \text{Cl}^-$ or Br^-), both summarizing published data and presenting a number of new, exciting results. The structural properties of $\text{Cu}_2\text{Cl}_6^{2-}$ dimers have been discussed as part of a review of the structural characteristics of ACuCl_3 salts (Willett and Geiser 1984) while a summary of known pseudo-planar $\text{Cu}_n\text{X}_{2n+2}^{2-}$ anions has recently appeared (Geiser *et al* 1986). The magneto-structural correlations in bibridged copper(II) halides were summarized some time ago (Willett 1985) but numerous other results have been obtained since that time, particularly for the $\text{Cu}_n\text{X}_{2n+2}^{2-}$ systems with $n = 3$ and 4, as well as for $\text{Cu}_2\text{Br}_6^{2-}$ dimers.

2. Magnetic behavior of $\text{Cu}_2\text{X}_6^{2-}$ dimers

2.1 Structural properties

Starting with the planar $\text{Cu}_2\text{X}_6^{2-}$ dimer (figure 1a), two possible distortions have been observed (Geiser and Willett 1984). One involves a twisted dimer (figure 1b) in which the copper(II) ion distorts towards a tetrahedral coordination geometry. The distortion is characterized by a twist angle, τ , between the bridging Cu_2X_2 plane and the terminal CuX_2 planes. The second involves a bifolded or "sedia" distortion, in which two terminal halide ions (one on each end of the dimer) are twisted out of the bridging plane. This distortion is characterized by a bifold angle, σ , between the central Cu_2X_2 plane and the terminal CuX_3 planes. Of interest

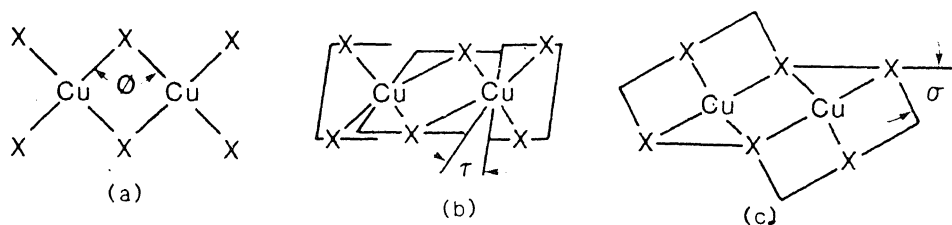


Figure 1. Distortions of the $Cu_2X_6^{2-}$ dimeric species. a) Planar; b) twisted; c) bifold or sedia.

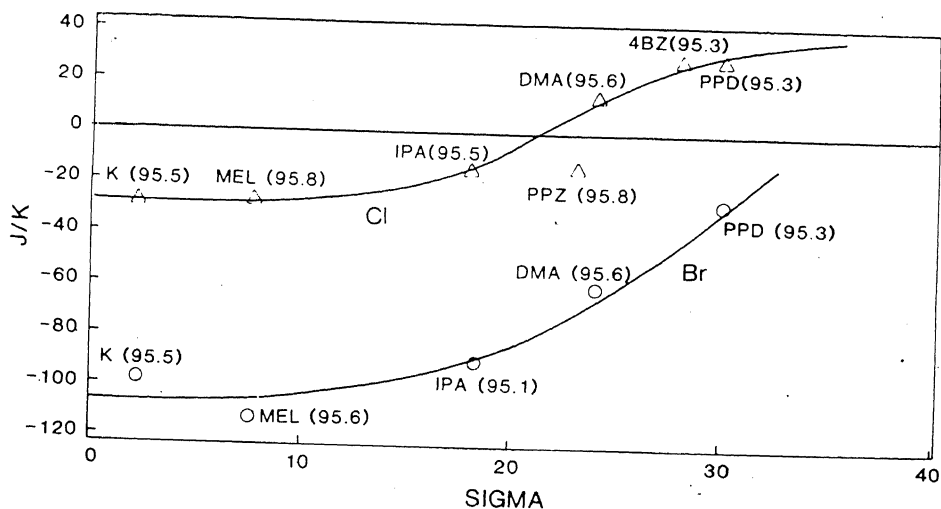


Figure 2. Plot of J/k vs bifold angle, σ , in $Cu_2Cl_6^{2-}$ and $Cu_2Br_6^{2-}$ dimers. (K = potassium, MEL = melaminium, IPA = isopropylammonium, DMA = dimethylammonium, PPZ = piperazinium, 4BZ = 4-benzylpiperidinium, PPD = piperidinium.)

magnetically, is the bridging Cu-X-Cu angle, ϕ . Thus, in discussing the magnetic properties of $Cu_2X_6^{2-}$ dimers, we are examining an exchange coupling hypersurface, which can be expressed as $J(\phi, \tau, \sigma, \dots)$. Among the other parameters affecting this complex surface will be the Cu-X distances, both within and between oligomers. Experimentally, it is desirable to study a series of systems where one, or at the most two, of these parameters vary.

The twisted dimers, with τ values typically in the range 40–50°, occur in structures where the dimers are structurally and magnetically isolated. The planar and sedia dimers generally occur in compounds where the dimers aggregate in stacks through the formation of 1 (sedia) or 2 (planar) semicoordinate Cu-X bonds per copper(II) ion between dimers. Two isolated planar dimers have been discovered in the last year (Honda *et al* 1985; Pellacani *et al* 1986). The range of the sedia distortion is substantial, going from $\sigma \sim 0$ out to $\sigma \sim 40^\circ$, with a large number of examples. In the sedia distortion, the *interdimer* Cu...Cl distance generally shortens as σ increases. Thus, in the limit or large σ , the copper(II)

coordination geometry approaches the trigonal bipyramidal limit. In the twisted dimers, $\phi \sim 93^\circ$, while in a majority of the planar or sedia dimers, $\phi \sim 95.5^\circ$ – 96.0° .

Calculations have been carried out by Hay *et al* (1978) as well as Bencini and Gatteschi (1978) for a series of distortions of dimeric species. Results of these calculations show, for example, that $|\epsilon_1 - \epsilon_2|$ increases as the bridging Cu–L–Cu angle, ϕ , increases when $\phi > 90^\circ$, in accord with the experimental observation of increasing antiferromagnetic character as ϕ is increased. For the twisted dimer, they also show that $\epsilon_1 = \epsilon_2$ at an intermediate value of the twist angle, τ . Thus, as τ increases from $\tau = 0$, the interaction is first predicted to become more ferromagnetic, reach a maximum value, and then decrease as $\tau \rightarrow 90^\circ$.

The dependence of exchange coupling on these distortions can be readily understood following simple orthogonality arguments. For the planar dimers, each localized unpaired electron lies in a d_{xy} -like antibonding molecular orbital. The unpaired electron density is substantially delocalized out into the P_σ orbitals on the ligands, with only a small contribution into the ligand Δ orbitals. Thus, for $\phi \sim 90^\circ$, the orbitals on the two copper centers will be nearly orthogonal, and a ferromagnetic interaction is anticipated from Hund's rule arguments. As ϕ increases, the overlap increases, giving an antiferromagnetic contribution to the exchange coupling. As the dimers distort from planarity, the lobes of the local metal orbitals no longer point directly at the ligands, so the contribution of the ligand orbitals in the magnetic orbitals is expected to decrease. Thus, there is less overlap of the two localized magnetic orbitals, decreasing the antiferromagnetic contribution. Hence, the coupling becomes more ferromagnetic, at least initially, as the distortion increases.

The magnetic susceptibility data for isolated dimers can be analyzed with a simple Heisenberg dimer model, perhaps including a mean field correction to account for weak interdimer contacts (Chow *et al* 1975). These are likely to be more important in bromide salts, due to its increased van der Waal's radius as compared to the chloride salts. The sedia dimers constitute alternating magnetic chains, with an intradimer exchange pathway, J , and an interdimer exchange pathway, J' . For J and $J' < 0$, expressions for $\chi(J, J')$ are available (Hall *et al* 1981). The value of $|J'|$ is generally smaller than the magnitude of $|J|$, since the semi-coordinate bonds are approximately perpendicular to the magnetic orbital and the differential overlap between magnetic orbitals on different dimers is quite small. Thus, the mean field dimer model can be used when one or both of J and J' are ferromagnetic. However, in the crossover region, where J changes from ferromagnetic to antiferromagnetic, $|J|$ and $|J'|$ can be of the same order of magnitude, which confuses the magnetostructural conclusion. This crossover region covers a relatively large range of σ values for the chloride salts, but is much smaller for the bromide salts. This makes the study of copper(II) bromides more rewarding. No model exists for the susceptibility of stacked, planar dimers, since three J' pathways exist between dimers. Fortunately, $|J'|$ is generally smaller than $|J|$ in these systems, so a mean field dimer model is usually appropriate. In addition, with $J < 0$, if all J' pathways have the same sign, spin frustration occurs, tending to cancel out effects of the interdimer interactions (see discussion of trimers). In any case, when $J < 0$, J is uniquely determined by $T_{\max}$, the temperature at which χ_m reaches a maximum with $T_{\max}$ in the range $1.20 J/k - 1.25 J/k$.

2.2 Twisted dimers

The structural and magnetic data for systems containing isolated, twisted dimers are summarized in table 1. In addition to the ferromagnetic $(\phi_4A)CuX_3$ salts ($A = P, As, Sb$) (Bencini *et al* 1985), the planar dimers in the (morpholinium) CuX_3 salts (Scott and Willett 1987) are included, as is the infinite $(CuBr_2)_n$ chain of tetrahedra in $[(C_2H_5)_2NH_2]_2Cu_4Br_{10} \cdot EtOH$ (Fletcher *et al* 1983). The morpholinium salts have oxygen atoms from the morpholinium ions forming weak semi-coordinate bonds to the copper(II) ions, thus the dimers approximate isolated ions. From table 1, it is seen that as the coordination sphere twists towards tetrahedral, the bridging angle, ϕ , decreases substantially. The exchange coupling is antiferromagnetic for $\tau = 0^\circ$, becomes ferromagnetic for $\tau \sim 50^\circ$, and becomes antiferromagnetic again for $\tau \sim 85^\circ$. The initial decrease in the antiferromagnetic contribution to the exchange is readily understood, since the sedita distortion will cause the magnetic orbitals to twist out of the bridging Cu_2Cl_2 plane, thus leading to a decrease in the overlap of the magnetic orbitals at the bridging halides. Calculations for the twisted dimer, assuming $\phi = \text{constant}$, showed that $\varepsilon_1 = \varepsilon_2$ at $\tau \sim 30^\circ$ (Hay *et al* 1978). Thus, a maximum ferromagnetic interaction is expected at that point, with the coupling becoming more antiferromagnetic as τ changes from that value. The experimental data certainly confirm that general behavior. Extended Huckel calculations performed in our laboratory for the actual geometries of the $\phi_4AsCuCl_3$ and ϕ_4PCuCl_3 salts indicate that the maximum ferromagnetic value is expected at an τ angle slightly larger than 50° . Further experimental examples at different τ values are needed to fill out this section of the exchange energy surface.

2.3 Sedita dimers

A substantial series of stacked $Cu_2X_6^{2-}$ dimers have been synthesized and studied (O'Brien *et al* 1986; Willett 1986; Scott and Willett 1986) in conjunction with Prof. G. C. Pellacani's laboratory in Modena, Italy. These are listed in table 2, where it is seen that a fairly densely packed $J(\phi, \sigma)$ surface exists with $\sigma \leq 40^\circ$ and $95^\circ < \phi < 98^\circ$. In general, for $\phi \sim 95.5^\circ$, J is antiferromagnetic for small values of σ and becomes ferromagnetic for $\sigma > 25^\circ$. These data are plotted in figure 2 for both the chloride and bromide salts. The general trend from the data is clear, although considerable scatter is seen. This presumably is due to small changes in

Table 1. Structural and magnetic parameters for twisted $Cu_2X_6^{2-}$ dimers.

	ϕ	τ	J/k
(Morpholinium) $CuCl_3$	95.8	0	43
$(\phi_4As)CuCl_3$	93.8 ^a	48.2	28
$(\phi_4P)CuCl_3$	93.2 ^a	50.0	55
$(\phi_4Sb)CuCl_3$	94.6	44.4	65
(Morpholinium) $CuBr_3$	—	0	120
$(\phi_4As)CuBr_3$	—	~50	28
$(\phi_4P)CuBr_3$	—	~50	37
$[(C_2H_5)_2NH_2]_2[Cu_4Br_{10} \cdot EtOH]$	84.3 ^b	84.9	-21

^a Chow *et al* 1975; ^b See Willett and Geiser 1984 and references therein;

^c Pellacani *et al* 1986.

Table 2. Structural and magnetic parameters of stacked planar or sedia $\text{Cu}_2\text{X}_6^{2-}$ dimers^a.

Cation	X = Cl					X = Br				
	ϕ (°)	Cu-Cl, bridging (Å)	σ (°)	J/k (K)	$\epsilon_1 - \epsilon_2$ (eV)	ϕ (°)	Cu-Br, bridging (Å)	σ (°)	J/k (K)	
K^+	95.5°	2.318	1.5°	-28	0.1153	—	—	—	-95	
2-amino-3-hydroxy- pyridinium ⁺	—	—	—	—	—	97.0	~2.460	~6.3	—	
$\text{CH}_2\text{OHCH}_2\text{NH}_3^{+b}$	95.9	2.312	13.8	-6	0.1182	95.7	2.456	14.9	-60	
Melaminium ²⁺	95.8	2.334	7.6°	-28	0.1140	95.6	2.468	7.5	-113	
$\text{Me}_4\text{enH}_2^{2+}$	96.4	2.322	17.9°	-23	0.1130	95.7	2.451	17.1°	-134	
$(\text{CH}_3)_2\text{CHNH}_3^+$	95.5	2.308	19.2°	-14	0.1125	95.1	2.446	18.3	-90	
Piperazinium ²⁺	95.8	2.324	23.2	-13	0.1093	—	—	—	—	
$(\text{CH}_3)_2\text{NH}_2^+$	95.6	2.326	23.6	~15	0.1018	—	—	—	-60	
Piperidinium ⁺	95.5	2.288	29.6	26	0.1042	—	—	—	-9	
$4-\phi\text{CH}_2\text{C}_3\text{H}_{11}\text{N}^+$	95.3	2.311	28.7	30	0.0916	—	—	—	—	
$\text{MeNH}_2\text{C}_3\text{H}_4\phi^+$	95.1	2.339	46.1	70	—	—	—	—	—	
Paraquat ²⁺	97.5	2.318	31.7	-19	0.111	—	—	—	-74	

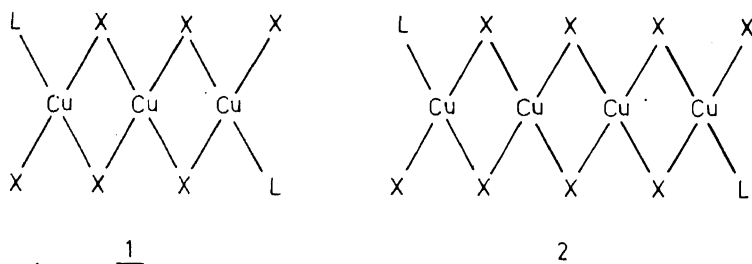
^a References therein; ^b The distortion in this salt yields a geometry closer to square pyramidal.

other geometrical parameters—e.g., bond lengths, non-bridging angles, semi-coordinate interactions, etc. This is borne out by extended Hückel calculation for the chloride salts (O'Brien *et al* 1986) in the spirit of the Hoffmann approach, where J_{AF} is proportional to $(\epsilon_1 - \epsilon_2)^2$. A comparison of the measured J/k values with the calculated $(\epsilon_1 - \epsilon_2)$ values in table 2 shows good correlation, even when the J/k vs σ correlation shows its largest scatter.

3. Magnetism of $\text{Cu}_3\text{X}_8^{2-}$ and $\text{Cu}_4\text{X}_{10}^{2-}$ oligomers

3.1 Structural properties

In addition to the dinuclear oligomers discussed in the previous section, we have prepared a large number of $n = 3$ (Grigereit *et al* 1986) and $n = 4$ oligomers (Rubenacker *et al* 1986; Halvorson *et al* 1986). These are characterized by the existence of pseudo-planar bibridged structures, 1 and 2 (Rubenacker *et al* 1986; Halvorson *et al* 1986), with $\text{X} = \text{Cl}^-$ or Br^- , or a neutral ligand. They are conveniently visualized as finite segments of the infinite chains present in

**Chart 1.**

the anhydrous CuX_2 salts. The $A_2Cu_nX_{2n+2}$ salts are synthesized by crystallization of the AX salt from aqueous and/or alcoholic solution with excess CuX_2 present. Within each oligomer, the copper ions have basically a square planar coordination geometry. The bridging $Cu-Cl-Cu$ angles range from 93° to 95° . Thus, an AFM exchange coupling is anticipated within the oligomers. As with the stacked dimers, the copper(II) ions within the oligomers complete their coordination sphere by forming one or two semi-coordinate bonds to halide ions in adjacent oligomers. The stacking patterns thus formed are shown in figure 3.

The magnetic behavior of the isolated copper(II) trinuclear species can be modeled by the nearest neighbour Heisenberg Hamiltonian

$$\mathcal{H} = -2J(S_1 \cdot S_2 + S_2 \cdot S_3), \quad (3)$$

which has energy levels $E_1 = 2J$ ($S = \frac{1}{2}$), $E_2 = 0$ ($S = \frac{1}{2}$), and $E_3 = -J$ ($S = \frac{3}{2}$). For AFM coupling ($J < 0$), the E_1 level lies low in energy. The susceptibility of the system is given by

$$\chi_M = N_1\chi_{1/2} + N_2\chi_{1/2} + N_3\chi_{3/2} \quad (4)$$

where N_i is the population of the i th level and χ_i is the molecular (4) susceptibility of a state with spin S .

For the tetramers, the data were fit to a nearest neighbor Heisenberg Hamiltonian,

$$\mathcal{H} = -2J_1(S_1 \cdot S_2 + S_3 \cdot S_4) - 2J_2(S_2 \cdot S_3),$$

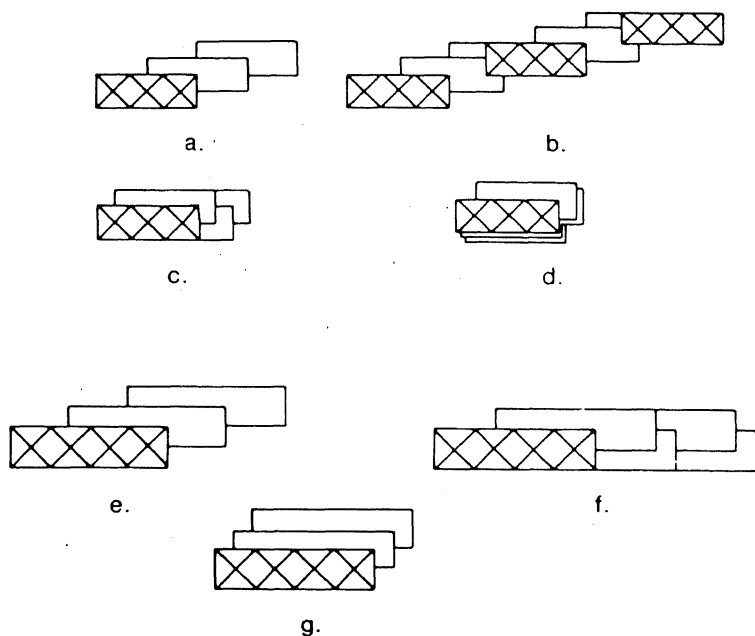


Figure 3. Stacking patterns for trimeric and tetrameric copper(II) halide oligomers.

where J_1 is the exchange constant between the outer pair of copper(II) ions and J_2 is the central exchange constant. This model has been solved exactly (Rubenacker *et al* 1986) and the magnetic susceptibility is given as

$$\begin{aligned} \chi = (N_0 g^2 \mu \beta^2 / kT) [& 10 \exp(-E_1/kT) + 2 \exp(-E_2/kT) \\ & + 2 \exp(-E_3/kT) + 2 \exp(-E_4/kT)] \\ & \times (1 - x)/Z + x N_0 g^2 \mu \beta^2 / kT, \end{aligned} \quad (5)$$

where Z is the partition function, x is the fraction of tetrameric impurity, and the energy levels and spin degeneracies are

$$\begin{array}{ll} E_1 = -J_1 - (1/2)J_2, & S_1 = 2, \\ E_2 = J_1 - (1/2)J_2, & S_2 = 1, \\ E_3 = (1/2)J_2 + [J_1^2 + J_2^2]^{1/2}, & S_3 = 1, \\ E_4 = (1/2)J_2 - [J_1^2 + J_2^2]^{1/2}, & S_4 = 1, \\ E_5 = J_1 + (1/2)J_2 + [4J_1^2 - 2J_1J_2 + J_2^2]^{1/2}, & S_5 = 0, \\ E_6 = J_1 + (1/2)J_2 - [4J_1^2 - 2J_1J_2 + J_2^2]^{1/2}, & S_6 = 0. \end{array}$$

3.2 Trimeric systems

We will first examine the magnetic behavior of $\text{Cu}_3\text{Cl}_6(\text{CH}_3\text{CN})_2$, which illustrates the expected behavior of a simple trimer system. It forms stacks as in figure 3b. Figure 4a shows a plot of χ_M vs T for $\text{Cu}_3\text{Cl}_6(\text{CH}_3\text{CN})_2$, while figure 4b gives a plot of $\chi_M T$ vs T for the same salt. The gradual depopulation of the quartet state predicted by the Boltzman distribution now is evident in figure 4b where the $\chi_M T$ data shows a gradual decrease initially as T decreases, then a more rapid decrease near $T = 50$ K, and then a leveling out at the expected $S = \frac{1}{2}$ value at low temperature. In the χ_M data, χ_M increases steadily as T is lowered. The theory reproduces this behavior very accurately. However, qualitatively different behavior is seen for salts which stack as in figures 3c or 3d. As seen in figures 5a and 5b, the value of $\chi_M T$ for $(3\text{MAP})_2\text{Cu}_3\text{Cl}_8$ stays more level at high temperature and drops more rapidly than predicted by the simple theory (dashed line, figure 7b). The χ_M data also shows this in that χ_M reaches a plateau where it stays essentially constant over a wide temperature range. Inclusion of a J_{13} term in (3) cannot reproduce this behavior. In essence, we are seeing evidence of a cooperative (non-Boltzman-like) behavior with the quartet state staying populated longer than expected. Other salts studied with similar stacking patterns show this behavior to a greater or lesser extent.

A possible explanation of this phenomenon may be related to the phenomenon of spin frustration. In 3 below, we see several possible spin arrangements between adjacent trimers in one stack of the type illustrated in figure 3a with intertrimer exchange pathways J' indicated. In 3b, the interaction between two ground spin $\frac{1}{2}$ states are considered. If all J' have the same sign, then the spin at site 1' is frustrated, i.e., it gets conflicting spin alignment messages via J_{11}' and J_{21}' . The same is true for the spin at site 2'. In 3c, the interaction between spin $\frac{1}{2}$ and spin $3/2$ states is depicted. Again, spins 1' and 2' are frustrated. However, this is not the

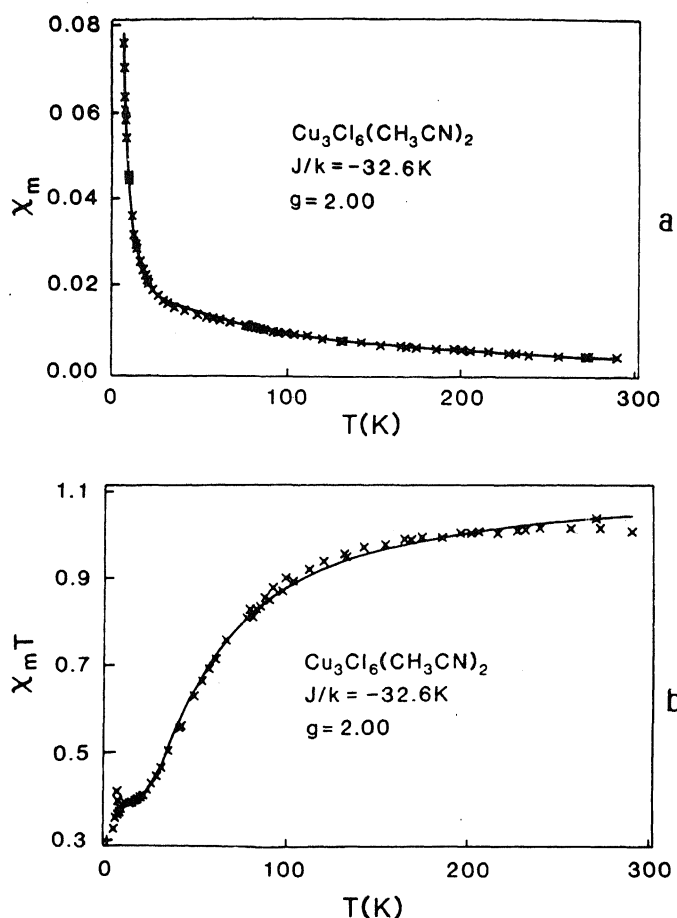


Figure 4. a. χ_M vs T for $Cu_3Cl_6(CH_3CN)_2$. b. $\chi_M T$ vs T for $Cu_3Cl_6(CH_3CN)_2$.

case for two adjacent spin $3/2$ states (3d) when J' is positive. Then the spin alignment information at sites $1'$ and $2'$ is consistent. Thus, it will cost less energy to form two adjacent $S = 3/2$ states than two isolated ones. That is, the population of the $3/2$ state stays larger than predicted by Boltzman statistics as long as it has an appreciable population. We can account for this in a phenomenological matter by applying a FM mean field correction to the quartet state (irrespective of the sign of J') as in (6),

$$\chi_M = N_1 \chi_{1/2} + N_2 \chi_{1/2} + N_3 \left[T/(T - \theta) \right] \chi_{3/2}. \quad (6)$$

This gives an excellent fit to the data, as given by the solid line in figure 5b.

The data for the salts studied are summarized in table 3. For the Cl salts, J/k ranges from $-20K$ to $-33K$. The AFM coupling in the Br salt studied is considerably larger ($-100K$), as observed in other AFM systems.

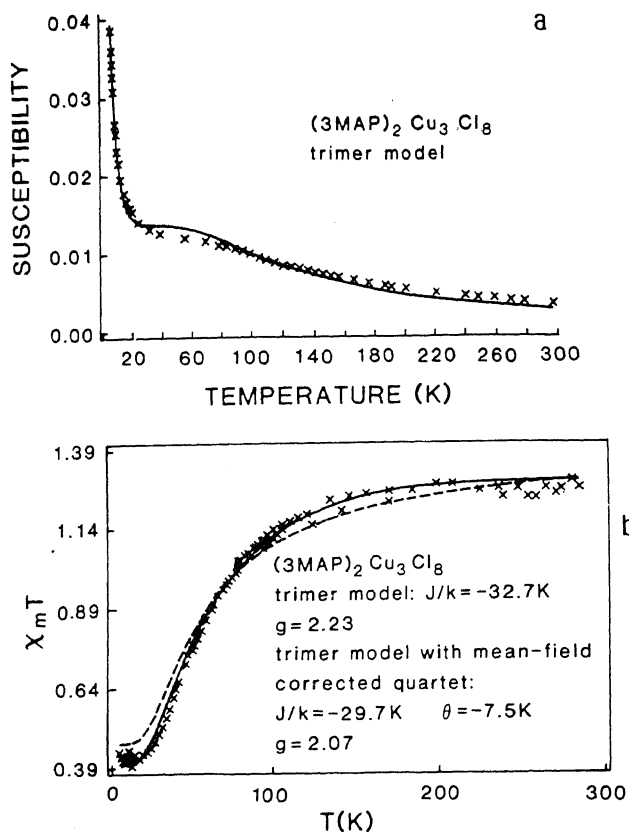


Figure 5. a. χ_M vs T for $(3\text{MAP})_2\text{Cu}_3\text{Cl}_8$. b. $\chi_M T$ vs T for $(3\text{MAP})_2\text{Cu}_3\text{Cl}_8$.

3.3 Tetrameric system

Three pseudo-planar $\text{Cu}_4\text{X}_{10}^{2-}$ systems have been studied, two chloride salts (Halvorson *et al* 1986) and one bromide salt (Rubenacker *et al* 1986). In each case, the central bridging angles ($\sim 93.5^\circ$) are smaller than the outer bridging angles ($\sim 94.5^\circ$). The magnetic data [figure 6 for $(\text{NMe}_4)_2\text{Cu}_4\text{Cl}_{10}$] is characteristic of antiferromagnetic coupling and exhibits the usual paramagnetic "impurity" tail. The data are very similar to that obtained from AFM dimers, and thus it is assumed that strong AFM coupling, J_1 , exists between the end pair of copper atoms and that weaker coupling, J_2 , exists between the central pair of copper atoms. Because of this strong AFM coupling between the end pairs, the spin system is essentially coupled at temperatures above which coupling between the central pairs becomes significant. This means that the data analysis is insensitive to the coupling between the central pairs. It is found that $J_1/k = -62\text{ K}$ for $(4\text{MAP})_2\text{Cu}_4\text{Cl}_{10}$, $J_1/k = -64\text{ K}$ for $(\text{NMe}_4)_2\text{Cu}_4\text{Cl}_{10}$, and $J_1/k = -180\text{ K}$ for $(\text{Me}_3\text{NH})_2\text{Cu}_4\text{Br}_{10}$. The stronger AFM coupling for the Br system is again noted.

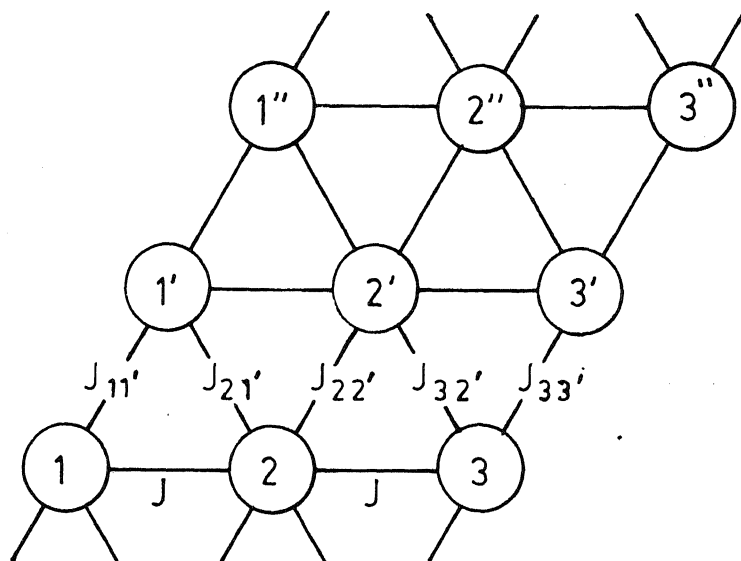
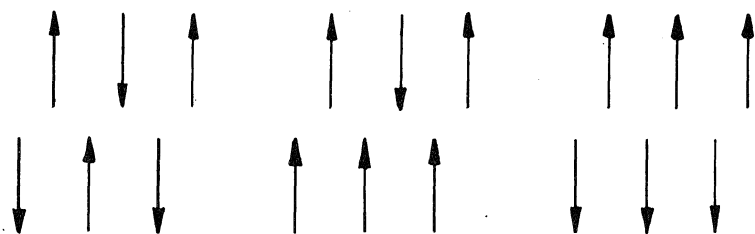
3a3b3c3d

Chart 2.

Table 3. Magnetic parameters for pseudo-planar bibridged copper(II) chloride trimers.

Compound	J/k_a	theta	g
NMPZ	-29.4(3)	-1.7(2)	2.183(7)
NMPA	-19.4(1)	-4.9(2)	2.053(7)
3MAP	-29.7(3)	-7.5(3)	2.067(9)
CH ₃ CN	-32.6(5)	0	2.004(4)

4. Discussion

In examining the data for the summarized series of symmetrically bibridged copper(II) chloride and bromide salts, discussed above, it is worthwhile examining the role of the bridging ligand. For most ferromagnetic salts in the series, the

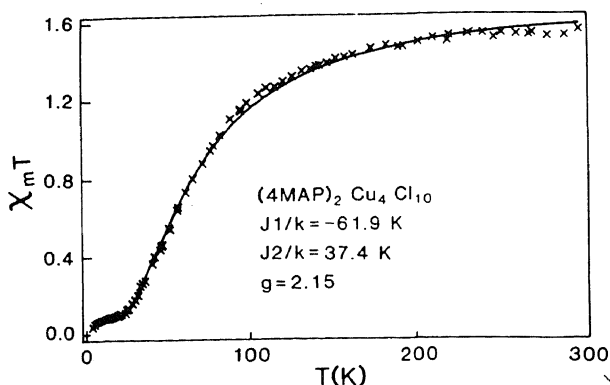


Figure 6. Plot of $\chi_M T$ vs T for $(4\text{MAP})_2\text{Cu}_4\text{Cl}_{10}$.

magnitude of J/k is approximately the same irrespective of the ligand. However, as the salts become antiferromagnetic, J/k decreases much more rapidly for the bromide salts than chloride salts. For those salts where structures are known for both the chloride and bromide analogs, little difference in the structures occur, other than those attributable to the larger ionic radius of the bromide ion. Thus, these trends cannot be accounted for by structural arguments. The cause can be readily seen, however, by examining the factors which affect the antiferromagnetic contribution to the exchange (Willett 1986). Hay *et al* (1978) argue that the value of $(\epsilon_1 - \epsilon_2)$ in (1) is inversely proportional to the difference in energies between the ligand orbitals and the magnetic orbital on the metal. This quantity may be estimated from the intense ligand-to-metal charge transfer transitions, which occur at the UV-visible borderline for the chloride salts ($\sim 25\text{--}30,000\text{ cm}^{-1}$) but are in the middle of the visible region for the bromide salts ($\sim 15\text{--}20,000\text{ cm}^{-1}$). Thus, it is expected that the antiferromagnetic contribution to the exchange, J_{AF} , will be 2–3 times larger for the bromide salts than for the chloride salts. This is in excellent agreement with the experimental trends, as can be seen in figure 7 where $J(\text{Cl})$ is plotted vs $J(\text{Br})$. A rough linear relationship is readily observed, with a slope of approximately $\frac{1}{2}$.

A comparison of the correlation of J/k values with oligomer size for pseudoplanar $\text{Cu}_n\text{X}_{2n+}^{2-}$ anions (table 4) reveals some very interesting, but unexpected, trends. It is observed that J tends to become more negative, while ϕ decreases, as n increases. For planar bibridged $\text{Cu}(\text{II})$ systems, it is well established that as the bridging Cu-X-Cu angle increases, J becomes more antiferromagnetic (Fletcher *et al* 1983; Willett 1986). From table 4, it is seen that the compound with the smallest angle, CuBr_2 , $\phi = 92.1^\circ$, has one of the strongest antiferromagnetic coupling constants, $J/k = -165\text{ K}$. Thus, additional factors must be operative to account for these trends. One parameter of significance is certainly the Cu-X bond lengths in the bridge, since the delocalization of the magnetic electron out onto the ligands decreases as the Cu-X distance increases. Thus, shorter distances should lead to stronger antiferromagnetic coupling due to increased overlap. The bridging Cu-X bond lengths in dimeric species are particularly long, since the *trans* effect of the shorter terminal Cu-X bonds causes *all* bridging bonds to be elongated. In

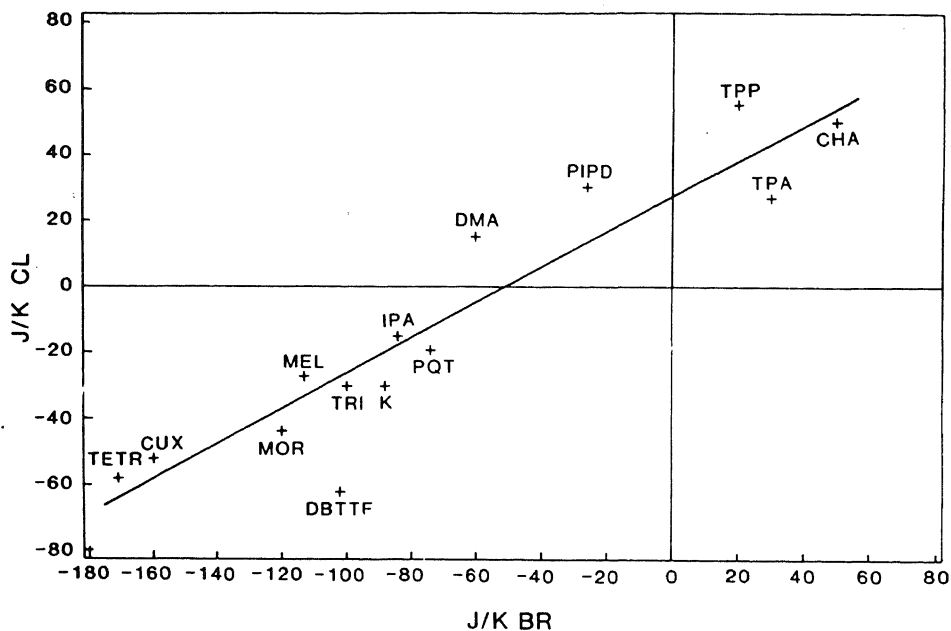


Figure 7. Plot of $J(Cl)$ vs $J(Br)$ for bridged copper(II) halide systems. (TETR = $Cu_4X_{10}^{2-}$ tetramers, $CuX = CuX_2$, MOR = morpholinium, MEL = melaminium, TRI = $Cu_3X_8^{2-}$ trimers, DBTTF = dibenzatetrathiafulvalenium, K = potassium, IPA = isopropylammonium, PQT = paraquat, DMA = dimethylammonium, TTP = tetraphenylphosphonium, TPA = tetraphenylarsonium, CHA = cyclohexylammonium.)

Table 4. J/k values for $Cu_nX_{2n+2}^{2-}$ oligomers.

n	X = Cl ⁻		X = Br ⁻	
	ϕ	J/k	ϕ	J/k
2	95.6°	-28 K	~96°	-95 K
3	94°	-30 K	94°	-100 K
4	94.5°	-60 K	94.8°	-180 K
∞	—	-55 K	92.1°	-165 K

trimers and tetramers; only half of the bridging Cu-X distances are elongated. Thus, an increase in antiferromagnetic contribution is expected for $n > 2$. Other effects must account for the difference between the exchange coupling for the trimers and the terminal bridges in the tetramer, as well as for the infinite chains. Possible effects include the unusually large terminal X-Cu-X angle, variations in the semi-coordinate Cu...X distances, and small deviations from non-planarity. Theoretical calculations to explore these factors are planned.

Acknowledgement

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Lanthanide perchlorate complexes of 2-acetamidopyridine-1-oxide

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Abstract. 2-acetamidopyridine-1-oxide (AcAmPyO) complexes of six lanthanide perchlorates, with the general composition $\text{Ln}(\text{AcAmPyO})_5(\text{ClO}_4)_3$, have been synthesized and characterized by analysis, molar conductance, infrared, proton NMR and electronic spectral data. Infrared and conductance studies indicate the ionic nature of the anion. The coordination of the ligand through the N–O and C=O moieties is shown by the infrared and proton NMR spectral analysis.

Keywords. Lanthanide perchlorate complexes; 2-acetamidopyridine-1-oxide; IR spectra; proton NMR; electronic spectra.

1. Introduction

A survey of the literature in the field of lanthanide coordination chemistry reveals that although lanthanide complexes with neutral bidentate pyridine-1-oxide ligands like picolinamide-1-oxide (Navaneetham and Soundararajan 1979) are known, pyridine-1-oxide ligands containing the $-\text{NHCOCH}_3$ (acetamido) group have not been employed for complexation with lanthanides. We report in this paper the synthesis and characterization of new perchlorate complexes of six lanthanides with 2-acetamidopyridine-1-oxide (AcAmPyO).

2. Experimental

2.1 Materials

2-aminopyridine was obtained from Aldrich Chemical Company, USA and used as such. Hydrated lanthanide perchlorates were obtained as reported earlier (Behrendt and Madan 1976).

2.2 Synthesis of AcAmPyO

2-aminopyridine (0.1 mol) was refluxed with freshly distilled acetic anhydride (0.11 mol) for two hours. Acetic acid and acetic anhydride were removed by distillation at 100 mm/Hg pressure. The solid residue was recrystallized from ether to get colourless plates of 2-acetamido pyridine (m.p. 66°C ; Lit. $66\text{--}7^\circ\text{C}$). The acetamidopyridine was then N-oxidised adopting the method described by Ochidi (1967)

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for the preparation of quinoline-1-oxide. The crude product was recrystallized from acetone m.p. 132°C (Lit. 131–32°C).

2.3 Preparation of the complexes

To a hot solution of AcAmPyO (12 mmol) in ethylacetate (50 ml), a solution of hydrated lanthanide perchlorate (1 mmol) also taken in ethylacetate (5 ml) was added with stirring. Stirring in the hot condition was continued for 10 minutes. The solvent was then decanted and the sticky mass thus obtained was washed thrice with hot chloroform (10 ml) to remove any unreacted ligand, washed twice with dry diethyl ether (15 ml), and finally dried *in vacuo* (≈ 3 mm/Hg) at 80–85°C for about 30 minutes to get the dry solid complex.

2.4 Analyses

The metal and anion contents in all the complexes were estimated as reported previously (Serra *et al* 1976); ligand was estimated spectrophotometrically at 230 nm using the calibration curve method.

2.5 Physical measurements

Conductance measurements in acetonitrile, infrared spectra in mulls, proton NMR spectra of the ligand and its La^{3+} complex in CD_3CN and electronic spectra both in solution (acetonitrile) and solid state (mulls) were obtained by the methods described previously elsewhere (Rajasekar and Soundararajan 1981).

3. Results and discussion

Analytical data for the newly prepared complexes listed in table 1 indicate that five molecules of the ligand are associated with each tripositive lanthanide ion $\text{Ln}(\text{AcAmPyO})_5(\text{ClO}_4)_3$. Molar conductance values in acetonitrile indicate that all the six complexes behave as 1:3 electrolytes (Geary 1971). The complexes are hygroscopic and soluble in polar solvents such as methanol, acetone, acetonitrile, DMSO and DMF but insoluble in CCl_4 , chloroform and benzene.

Table 1. Analytical and molar conductance data for the AcAmPyO complexes of lanthanides.

Complex	Metal (%)		Ligand (%)		ClO_4^- (%)		Λ_M^+
	Found	Calcd.	Found	Calcd.	Found	Calcd.	
$\text{La}(\text{AcAmPyO})_5(\text{ClO}_4)_3$	14.48	11.60	62.53	63.48	24.80	24.92	389.2
$\text{Nd}(\text{AcAmPyO})_5(\text{ClO}_4)_3$	11.87	11.99	62.56	63.19	—	—	363.8
$\text{Gd}(\text{AcAmPyO})_5(\text{ClO}_4)_3$	12.80	12.94	61.89	62.52	—	—	350.2
$\text{Dy}(\text{AcAmPyO})_5(\text{ClO}_4)_3$	13.18	13.31	61.75	62.25	24.38	24.44	342.3
$\text{Ho}(\text{AcAmPyO})_5(\text{ClO}_4)_3$	13.36	13.48	61.52	62.13	—	—	348.8
$\text{Yb}(\text{AcAmPyO})_5(\text{ClO}_4)_3$	13.93	14.05	61.10	61.72	—	—	349.8

⁺ Molar conductance in acetonitrile ($\text{Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

3.1 IR spectra

The presence of a very strong band in the region 1085–1105 cm⁻¹ (ν_3) and a medium unsplit one in the region 620–622 cm⁻¹ (ν_4) in the IR spectra of all the complexes (table 2) confirms evidence of non-coordinated perchlorates from conductivity measurements. Coordination of the perchlorate groups would result in a lowering of the symmetry from T_d symmetry and a splitting of these bands.

The shifts in $\nu_{\text{N-O}}$, amide I and amide II, $\delta_{\text{N-O}}$ and the $\gamma_{\text{C-H}}$ bands of the ligand in the complexes indicate the coordination of the N-oxide and C=O groups of the ligand to the tripositive lanthanide ion. The $\nu_{\text{N-O}}$ and the amide I bands are lowered by 5 cm⁻¹, while the amide II, $\delta_{\text{N-O}}$ and $\gamma_{\text{C-H}}$ bands are shifted to higher frequencies by 5, 10 and 15 cm⁻¹, respectively, in the complexes. These positive shifts amply demonstrate a decrease in the π -electron density of the amide groups and the heterocyclic ring as a result of the bidentate binding of the ligand, through the N-oxide and amide carbonyl groups, to the lanthanide ion.

3.2 Proton NMR spectra

Additional evidence for the coordination of the ligand is provided by the proton NMR spectra of the ligand and La³⁺ complex (diamagnetic). The spectral data are given in table 3. The downfield shifts of all the ring proton signals observed in the La³⁺ complex (compared to the ligand) concomitantly prove the coordination of the ligand to the metal ion via the N–O and C=O groups.

3.3 Electronic spectra

The electronic spectral assignments of Nd³⁺ and Ho³⁺ complexes along with their *J*-level assignments are presented in table 4.

Table 2. Important infrared frequencies (in cm⁻¹) and their assignments for AcAmPyO and its complexes.

Ligand	La	Nd	Gd	Dy	Ho	Yb	Assignment
3175–	3325–	3300–	3300–	3325–	3325–	3325–	ν_{NH}
3400 <i>wb</i>	3425 <i>wb</i>	3400 <i>wb</i>	3400 <i>wb</i>	3425 <i>wb</i>	3425 <i>wb</i>	3425 <i>wb</i>	
1710 <i>s</i>	1705 <i>m</i>	1702 <i>m</i>	1702 <i>m</i>	1705 <i>m</i>	1708 <i>m</i>	1705 <i>m</i>	Amide I
1575 <i>m</i>	1580 <i>m</i>	1580 <i>m</i>	1582 <i>m</i>	1580 <i>m</i>	1585 <i>m</i>	1580 <i>w</i>	Amide II
1278 <i>m</i>	1270 <i>w</i>	1270 <i>w</i>	1270 <i>w</i>	1270 <i>w</i>	1270 <i>w</i>	1275 <i>w</i>	$\nu_{\text{N-O}}$
—	1090 <i>s</i>	1090 <i>s</i>	1090 <i>s</i>	1090 <i>s</i>	1105 <i>s</i>	1085 <i>s</i>	$\nu_3\text{ClO}_4$
860 <i>w</i>	870 <i>w</i>	870 <i>w</i>	870 <i>w</i>	870 <i>w</i>	865 <i>w</i>	865 <i>w</i>	$\delta_{\text{N-O}}$
745 <i>w</i>	755 <i>w</i>	755 <i>w</i>	758 <i>w</i>	755 <i>w</i>	760 <i>w</i>	758 <i>w</i>	$\gamma_{\text{C-H}}$
—	620 <i>m</i>	620 <i>m</i>	620 <i>m</i>	622 <i>m</i>	621 <i>m</i>	620 <i>m</i>	$\nu_4\text{ClO}_4$

Abbreviations: *w* = weak; *s* = strong; *m* = medium; *b* = broad.

Table 3. Proton NMR spectral data for AcAmPyO and its La³⁺ complex in CD₃CN (chemical shifts in δ w.r.t. TMS).

Compound	3H	4H	5H	6H
AcAmPyO	6.97	7.22	6.69	8.18
La ³⁺ complex	7.03	7.34	6.71	8.27

Table 4. Electronic spectral data for AcAmPyO complexes of Nd³⁺ and Ho³⁺

Nd ³⁺		Ho ³⁺	
<i>J</i> level	Energy(KK)	<i>J</i> level	Energy(KK)
⁴ G _{7/2}	19.05	⁵ F ₁ ' ⁵ G ₆	22.15
⁴ G _{5/2} ' ² G _{7/2}	17.13	⁵ F ₃	20.31
β =	0.9942	β =	0.9928
δ =	0.5870	δ =	0.7239

The various bands exhibit red shifts with respect to the aquo ion and the nephelauxetic shifts are in the range found for many lanthanide complexes. Sinha (1966) has proposed a δ scale to express and metal-ligand covalency, which is given by the relation

$$\delta(\text{percent}) = [(1-\beta)/\beta] \times 100,$$

where β is the average value of $\nu_{\text{complex}}/\nu_{\text{aquo}}$. The positive values of δ suggest a certain amount of covalency in the metal-ligand band in the six lanthanide complexes. The shapes of the hypersensitive bands resemble those of the ten coordinate lanthanide nitrate complexes of 2-N-acetylaminopyridine (Rajasekar 1980). The marked similarities in the positions and the shapes of the bands in the solid state and in solution point to similarities in the coordination environment around the lanthanide ions in both the states and, hence, the compatibility in the solid state properties such as infrared and solution properties as well as conductivity and proton NMR.

On the basis of these available pieces of evidence a tentative coordination number of ten can be suggested for all the six lanthanide perchlorate complexes of AcAmPyO.

Acknowledgements

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Solvent extraction of metals using LIX26 extractant

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Abstract. Solvent extraction of some selected metals from an aqueous buffered solution by LIX26 extractant has been studied. The $pH_{1/2}$ values (at which 50% of metal ion is extracted) for extracting different metals by 1 v/v% LIX26 extractant in methyl isobutyl ketone have been obtained. The order of extraction of metals by LIX26 extractant as a function of $pH_{1/2}$ value is $Pd(II) < Cu(II) < Sb(III) < Fe(II) < Co(II) < Zn(II) < Ni(II) < Pb(II) < Mn(II) < Cd(II)$.

Keywords. LIX26 extractant; $pH_{1/2}$ values; hydrometallurgy.

1. Introduction

The major breakthrough in solvent extraction studies is the development of reagents known as chelating extractants (Ashbrook 1975). Among these extractants, compounds marketed under the trade name "LIX" reagents (Liquid Ion Exchange Reagent) by Henkel Corporation have assumed great importance in the hydrometallurgy of copper (Burkin 1983). These chelating extractants effect efficient and economical separation of copper from virtually all other metals in solution under a wide range of conditions. Very little information is available on the extraction of metals other than copper using LIX extractants. In the present paper, extraction of copper(II), antimony(III), zinc(II), cadmium(II), cobalt(II), nickel(II), manganese(II), palladium(II), lead(II), iron(II), and rhodium(III) with LIX26 extractant has been investigated. Such a study would be helpful in providing basic information required for hydrometallurgical separations and in the development of new analytical methods.

2. Experimental

2.1 Materials

LIX26; HL (containing substituted oxine in kerosene) was kindly supplied by Henkel Corporation, USA. The pH of the aqueous phase was maintained by using mixtures of potassium chloride-hydrochloric acid for pH 1-3, sodium acetate-acetic acid for pH 4-6, ammonium chloride-ammonia for pH 8-10, and ammonium acetate-ammonia for pH 6-8. A constant ionic strength in the aqueous phase was maintained by using potassium nitrate solution. Potassium chloride was used to

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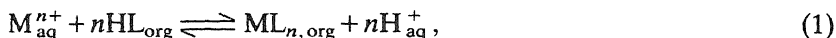
maintain ionic strength where hydrochloric acid was used. Analytical reagent grade methyl isobutyl ketone was used without further purification.

2.2 Extraction procedure

Ten millilitres of an aqueous layer containing an aliquot of metal solution, 5 ml of buffer solution and 1 ml of 1 M potassium nitrate solution was equilibrated with 10 ml of organic layer containing 1 v/v% LIX26 in methyl isobutyl ketone (MIBK). The mixture, in a stoppered bottle, was shaken in a wrist-action mechanical shaker for a period sufficient for the attainment of equilibrium at $35 \pm 1^\circ\text{C}$. After equilibration, pH of the aqueous phase was measured by an expanded scale pH meter (ECIL, India). In the case of extraction from more acidic solutions, hydrochloric acid solution of different molarities was used for attaining the desired concentration of acid in the aqueous phase. The concentration of metal in the aqueous layer was then measured by an SP 191 Pye Unicam Atomic absorption spectrophotometer.

3. Results and discussion

The extraction of a metal ion with a chelating ligand having a replaceable hydrogen ion may be represented by the following equation (Marcus and Kertes 1969).



where HL = LIX26 extractant.

The extraction constant (equilibrium constant) of this reaction is given by

$$K_{\text{ex}} = D[\text{H}^+]_{\text{aq}}^n / [\text{HL}]_{\text{org}}^n, \quad (2)$$

where distribution coefficient D is equal to the ratio $[\text{ML}_n]_{\text{org}} / [\text{M}^{n+}]_{\text{aq}}$. Equation (2) may be rewritten in the logarithmic form

$$\log K_{\text{ex}} = \log D - n\text{pH} - n \log [\text{HL}]_{\text{org}}, \quad (3)$$

Since the LIX26 extractant was supplied to us in a diluted form, the concentration of the extractant was taken on a v/v% basis. At a fixed concentration of the extraction the equilibrium constant (K_{ex}) is proportional to $\text{pH}_{1/2}$ values. The trend in K_{ex} values is known by knowing the trend in $\text{pH}_{1/2}$ values even though the absolute concentration of extractant is not known. LIX reagents used as extractants in commercial solvent extraction operations have, of necessity, to be produced on a large scale and do not have the purity of analytical reagents. It is not advisable (Ashbrook and Ritcey 1984) to do the initial work with refined or purified material in acquiring accurate data and then pilot the process using the commercially available material. In such studies impurities in reagents could render the work useless, since the extraction characteristics could be quite different using a pure material.

The data on the extraction of metals by LIX26 1v/v% in MIBK as a function of $\text{pH}_{1/2}$ values are given in table 1. This agrees partly with the extraction data reported by Sary (1968) for 0.01 M oxine-chloroform solutions as given in table 1. Gentry and Sherrington (1950) also report an order of extraction of metals by oxine

Table 1. Extraction data of some metals using 1 v/v% LIX26 extractant in MIBK.

Metal	pH _{1/2} (50% extraction)	pH for complete extraction	Shaking (min)	pH _{1/2} 0.01 M oxine in CHCl ₃ [†]
Mn(II)	6.75	≥ 7.9	30	6.66
Co(II)	5.00	6.7	30	5.08
Ni(II)	6.15	≥ 7.8	30	3.16
Cd(II)	6.95	≥ 8.6	60	6.65
Zn(II)	5.40	≥ 6.7	30	5.20
Cu(II)	Complete extraction in the pH range 1.5–9		5	1.77
Pb(II)	6.40	≥ 8.5	30	6.04
Sb(III)	< 1.5	1.5	30	—
Rh(III)	only 25% extraction		120	—
Fe(II)*	3.8	≥ 5.0	60	—
Pd(II)	< 1	—	30	< 0

* Chloroform as solvent; [†] Stary (1968)

as a function of pH_{1/2} values. It seems most likely that the extraction of metals by LIX26 extractant will generally follow that for metal oxinates. Since LIX26 resembles oxine in its extractive properties towards metals, it seems reasonable to suppose that similarities exist in their properties. There is also good agreement between extraction studies with LIX26 and Kelex 100 extractants. LIX26 possesses a K_{DR} of 3 orders of magnitude larger and a rather small K_a value than does oxine (Bag and Freiser 1982). Hence LIX26 offers an opportunity to study the mechanisms of metal extraction in acidic system not possible with oxine because of its low hydrophobicity as compared to LIX26 extractant.

The pH isotherms of LIX26 extractant with these selected metals are shown in figure 1. The order of extraction of metals by LIX26 extractant as a function of pH_{1/2} values is as follows:

Pd(II) < Cu(II) < Sb(III) < Fe(II) < Co(II) < Zn(II) < Ni(II) < Pb(II) < Mn(II) < Cd(II).

Except for Ni(II) and Cd(II) all the extraction data for LIX26 systems agree well with oxine systems (Stary 1968). Cadmium(II) forms hydrated complexes with oxine (CdL₂2HL) and with Kelex 100 forms complexes of the type CdL₂ (Lakshmanan *et al* 1974). Since hydrated complexes are better extracted into oxygenated solvents, cadmium extraction with LIX26 is effected at higher pH values as compared to oxine.

The order of extraction of metals by Kelex 100 as a function of pH_{1/2} value has been given as (Ma and Freiser 1984; Zhu and Freiser 1983):

Pd(II) < Cu(II) < Ni(II).

The extraction behaviour of these selected metals by LIX26 extractant can be briefly summarised as follows:

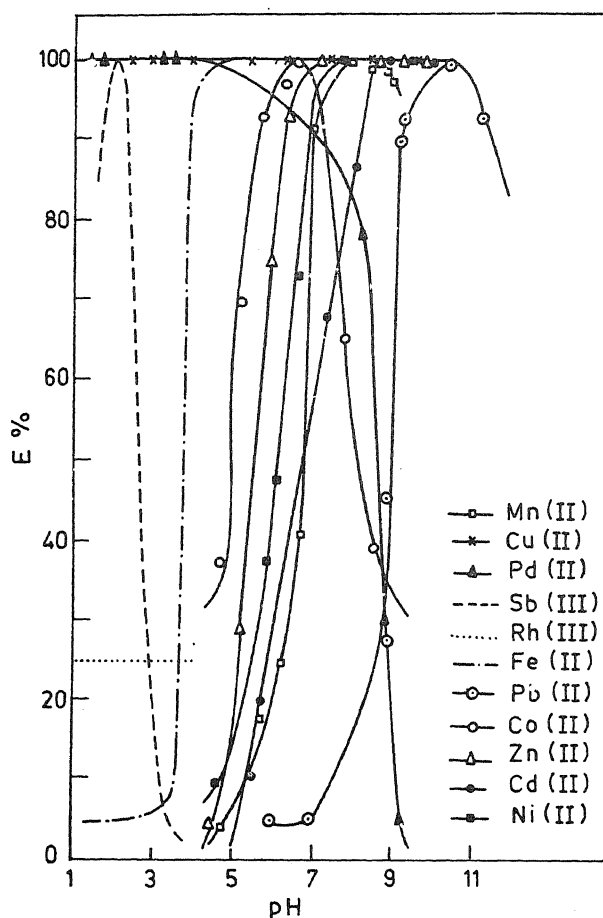


Figure 1. The pH isotherms of some selected metals using 1% v/v LIX26 extractant in MIBK. In case of Pb(II) the X-axis has been shifted by 2.0 pH units towards the +ve direction.

(i) Copper(II), antimony(III) and palladium(II) are extracted from acidic solutions. Antimony(III) gets extracted around pH 9 (Sandell 1959) with oxine, whereas with LIX26 an effective complete extraction is possible around pH 1.5. Palladium is extracted from highly acidic solutions thereby providing high selectivity in the recovery and purification of palladium. Effective separation of palladium is also achieved from nickel using this extractant.

(ii) Maximum extraction shown by rhodium(III) was only 25% above which no extraction was possible. At higher pH values extraction of cobalt(II) falls rapidly.

(iii) Complete extraction of copper(II), manganese(II), nickel(II), zinc(II), lead(II), cadmium(II) and iron(II) by using LIX26 extractant is around pH 8-6, though copper(II) is also extractable from acidic solutions.

Thus a single extraction at pH 8-6 from a dilute solution of metals into a smaller volume of the organic solvent will be a rapid and effective method of preconcentration of metals before atomic absorption spectrophotometric deter-

mination (Cresser 1978). Since LIX26 is soluble to a good extent in many organic solvents, both microscale as well as macroscale operations are possible.

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Quantitative estimation of substances spotted on filter paper by photoacoustic spectroscopy⁺

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Abstract. Quantitative estimation of coloured as well as colourless substances spotted on filter paper has been carried out by means of photoacoustic spectroscopy. The technique should be specially useful in the estimation of biological substances.

Keywords. Photoacoustic spectroscopy; quantitative estimation of spots on filter papers.

1. Introduction

Advantages of photoacoustic spectroscopy (PAS) in the study of materials, normally inaccessible to conventional optical spectroscopic techniques, have been described by various workers in the last few years (Rosencwaig 1980; Ganguly and Rao 1981; Tam 1986). Opaque and light scattering materials such as powders have been studied by Rosencwaig (1975). Adams *et al* (1980) have studied the quantum efficiency of solid fluorescent materials. Phase transition studies have been carried out by Florian *et al* (1978) and Somasundaram *et al* (1986a). Recently, Jagannathan *et al* (1982) have shown that PAS can be used for the study of surface acidities of solid oxide catalysts. Busse and Orgaback (1980) have used PA effect for depth profiling studies. Even biologically important materials have been studied by PAS. For example, Cahen *et al* (1978) have studied photosynthesis of chloroplast membranes; Balasubramanian *et al* (1984) have studied malaria parasites; Somasundaram *et al* (1986b) have studied the pigments in the thermophilic fungi.

The technique has been used for qualitative estimation of substances adsorbed on thin layer chromatograms by Rosencwaig (1975). Achwal *et al* (1984), however, have carried out quantitative estimation of 5-methylcytosine present in the DNA of *Drosophila melanogaster* by making use of a sensitive immunochemical assay and PA spectroscopy. These authors have used nitrocellulose paper for spotting the DNA and analysed the spectra for estimating the amount present. We considered it most worthwhile to investigate whether PAS was suitable for the quantitative estimation of substances spotted on ordinary filter papers, since a successful demonstration of such an application would open up a new dimension in analytical methods, especially in the case of biological substances. Estimation of substances spotted on filter paper would also serve to demonstrate one of the quintessential advantages of PA spectroscopy.

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2. Experimental

A single beam PA spectrometer described earlier elsewhere by Ganguly and Rao (1981) was used for this study. The light source was a 450 W high pressure xenon lamp. The light beam was modulated by a mechanical chopper and focussed into the cell by an adjustable mirror so that various areas of the sample could be investigated. For all the spectra obtained the conditions were as follows: scanning speed 100 nm/min; spectral resolution 20 nm; and chopping frequency 37Hz. The sample holder was modified in such a way as to accommodate filter papers without

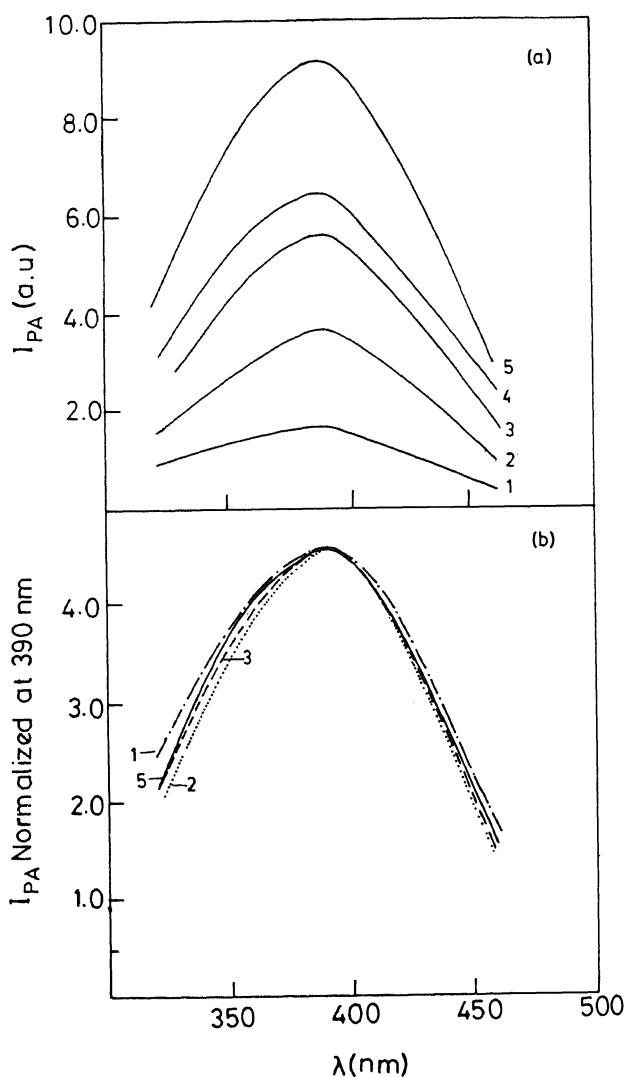


Figure 1. a) Normalized PA spectra of different amounts of *p*-nitroaniline spotted on Whatman-41 filter paper. 1: 1×10^{-3} M; 2: 2.5×10^{-3} M; 3: 5.0×10^{-3} M; 4: 7.5×10^{-3} M; 5: 1×10^{-2} M. b) Same spectra after equalizing intensities at 390 nm.

appreciable loss in signal. As usual normalization of recorded spectra were carried out using carbon black power spectrum.

Filter papers used were Whatman-40, 42 and 41. The filter paper was spotted using a micro syringe using either aqueous or alcoholic solutions of the substances. The diameter of the spots did not exceed 3 mm (illumination covered the spots fully). Different concentrations of solutions were used for spotting different amounts, keeping the quantity of liquid spotted the same for one series of experiments (either 2 or 5 μ l). Different volumes of the solutions of the same substance, containing the same weight of substance were also spotted to see whether there was any volume effect. For *p*-nitroaniline and other UV absorbing species, spotting was done either under UV light or on cut-out pieces of filter paper. Blank filter paper pieces were used to record background contribution and they were subtracted from the signal at every wavelength before reporting. The compounds studied were *p*-nitroaniline, crystal violet, neutral red, cytosine and L-tyrosine.

3. Results

In figure 1a we show the carbon black normalized PA spectra of *p*-nitroaniline at various concentrations spotted on Whatman-41 filter paper after subtracting background signals due to the filter paper. After equalizing the intensities of various spectra at 390 nm (corresponding to various concentrations) the same spectra are replotted in figure 1b. One sees that all the spectra are superimposable. Similar results are obtained for the substances studied and the normalized PA spectra of all of them are shown in figure 2.

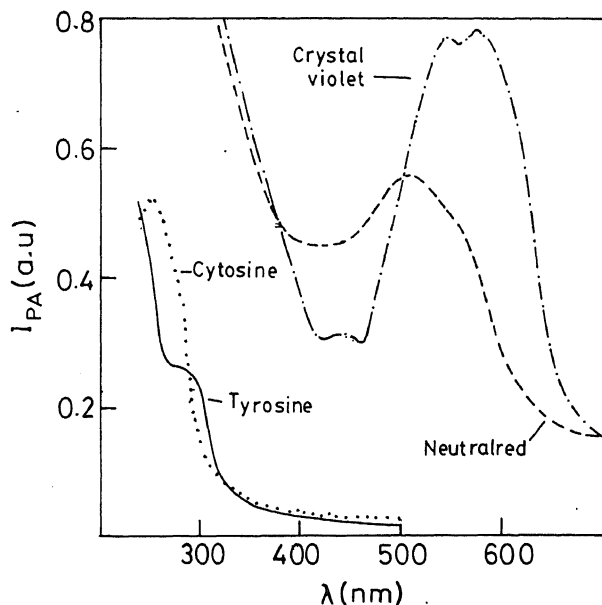


Figure 2. Normalized PA spectra of some compounds spotted on Whatman-41 filter paper.

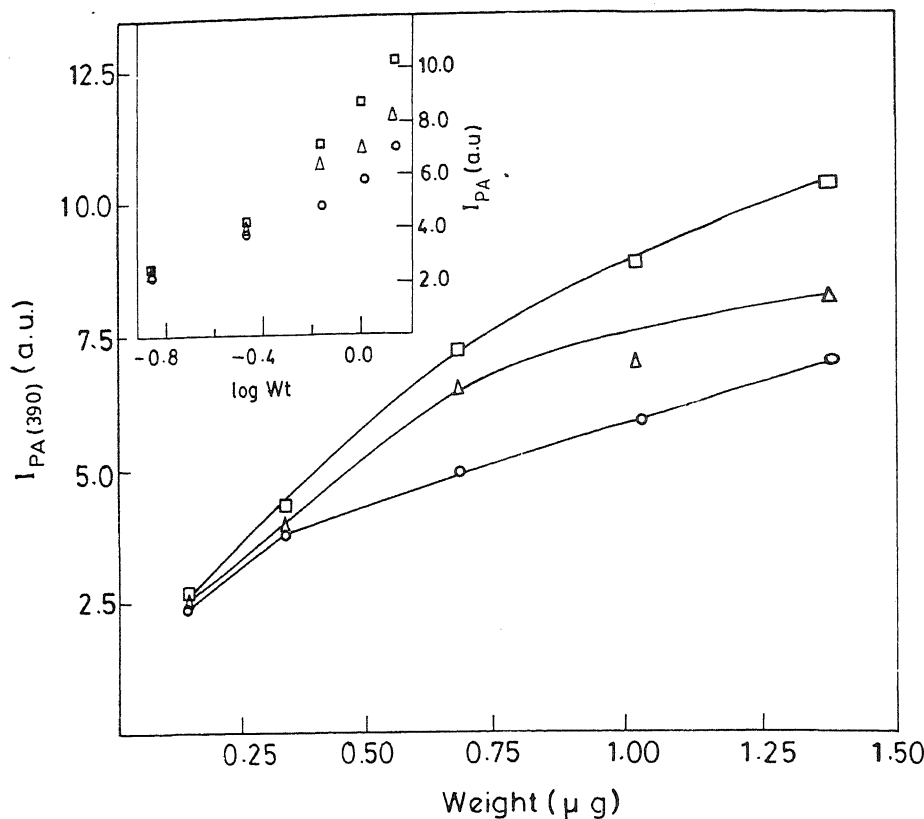


Figure 3. I_{PA} vs weight plot of *p*-nitroaniline spotted on three different filter papers. Circles, Whatman-41; triangles, Whatman-40; squares, Whatman-42. Inset shows I_{PA} vs log weight plots of the same spots.

In figure 3 we show the variation of PA intensity (I_{PA}) of *p*-nitroaniline at 390 nm for various amounts spotted on three different types of filter paper. We note that the intensities are not linearly related to the concentrations. Secondly, the intensity is greater when the filter paper is of finer grain size. For coarse grain filter paper, I_{PA} vs weight (wt.) of the substance, the plot is nearly linear in the high concentration regime. In figure 4 we show the variation of I_{PA} vs. wt. for other substances spotted on Whatman-41 filter paper. One sees a linear relationship between the intensity and concentration.

4. Discussion

The present study shows that there is a definite proportionality of I_{PA} to the wt. of the substance spotted on filter paper. To quantify this relationship, PA spectra has to be checked for saturation effects, as otherwise, increase in the amount may not bring about an increase in I_{PA} . It is seen from figure 1b that all the spectra are superimposable on one another indicating that even at the highest concentration studied there is no sign of saturation; furthermore, background subtraction

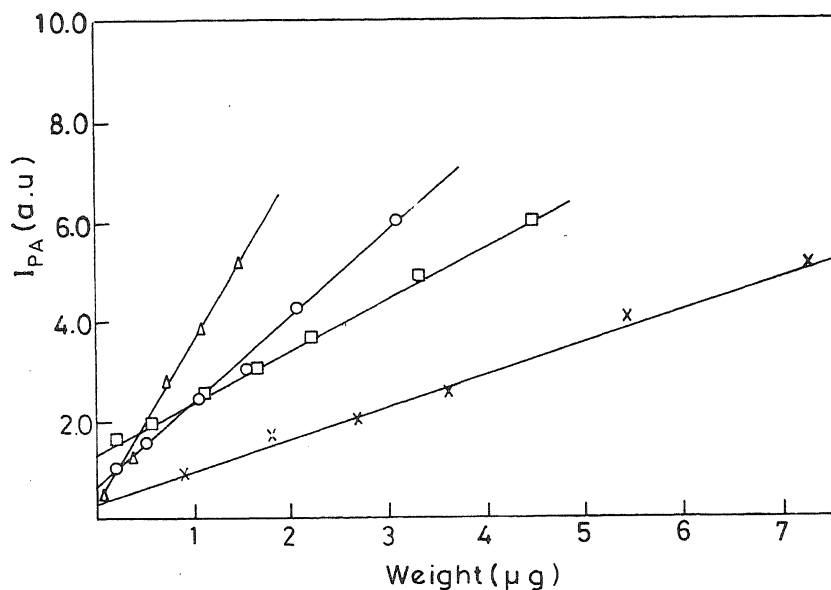


Figure 4. I_{PA} vs weight of various substances spotted on Whatman-41 filter paper at the absorption maxima of the unnormalized spectra. Circles, crystal violet (580 nm); triangles, neutral red (520 nm); squares, cytosine (280 nm); crosses, L-tyrosine (290 nm).

does not result in any artifacts. This indicates that one can correlate I_{PA} with concentration up to a concentration range. Normalized PA spectra shown in figure 2 resemble that of standard spectra of these substances showing that in the present case the spectra have not changed significantly even under conditions of adsorption. With a proper calibration curve we can, therefore, use PAS for the quantitative estimation of substances spotted on filter paper.

The nearly linear dependence obtained with Whatman-41 filter paper (figure 4) may be exploited to advantage in the sense that the number of calibration points is reduced. This technique will undoubtedly be of great value in biology where quantitative estimation of substances spotted on filter paper often poses difficulties. Another important feature is the minimum detectable amount of the substances spotted, which in our case is of the order of a few hundred nanograms. This can be gainfully used to estimate materials which are present in very small amounts and/or

The non-linear dependence of I_{PA} on wt. (figure 3) observed is likely to be due to particle size and light scattering effects. This has been discussed, in the case of powder, in some detail by Monahan and Nolle (1977) and recently by Monchalín *et al* (1984). Similar non-linear behaviour of the amount of light absorbed by paper containing various dyes has been pointed out by Foote (1939) and analysed by Van den Akker (1968). These authors have found, in the case of dyes adsorbed on papers, that with decreasing amounts of the dye the scattering increases. This may explain the non-linear part in the low concentration region. Since background contribution to the signal can vary with the size of the dye spot, one has to exercise caution while spotting. Spots, where weight of substance spotted is held constant but volume varied, did not show any difference in I_{PA} . One can clearly see

that only the solvent front advances, leaving the same sized spot in all the cases irrespective of the volume used. In our case where substances are spotted on filter paper, the absorbing chromophore is present as a thin layer on a substrate which is transparent to the radiation employed. Little is known about the generation of PA signals in such systems where the thermal properties of the substrate dominate the amplitude of the PA signal even though it is transparent to radiation (and hence inherently PA inactive). Systems such as these like solid catalysts, thin-layer chromatograms, substances adsorbed on filter papers have not been completely understood either from the theoretical or the experimental point of view. We are engaged at present in such studies.

The fraction of light absorbed seems to roughly show a logarithmic dependence on absorption coefficient, β . Melamed (1963) proposed a theory of scattering of light by particulate matter, from which the fraction of light absorption seems to show a logarithmic dependence on β for a considerable range of $\beta\delta$ ($10^{-3} \leq \beta\delta \leq 10^\circ$), where δ is the particle diameter. We do indeed find a nearly linear logarithmic dependence between I_{PA} and log wt. as shown in the inset of figure 3. This dependence could be usefully employed for the purpose of calibration and estimation.

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Preconcentration of iodide from saline water samples and determination by the catalytic method

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Abstract. A method is described for the determination of nanogram levels of iodide in saline water samples. The interfering chloride, present in milligram levels, is eluted out of a column of a strong anion exchanger, retaining the iodide quantitatively. The iodide is then recovered from the column with 2 M ammonium nitrate solution. The determination is carried out by the catalytic method based on the reduction of Ce(IV) by As(III) in presence of iodide. The arresting method was found to be more sensitive. The method can be easily adapted in a field laboratory, with accuracy comparable with neutron activation analysis.

Keywords. Iodide; saline waters; preseparation; catalytic method.

1. Introduction

Preconcentration of iodide from drinking water and common salt samples followed by its determination by neutron activation analysis was reported by us earlier (Krishnamoorthy and Iyer 1983). The short half-life of I-128 (25 min) necessitates that the laboratory should be situated close to the nuclear reactor. Hence this method cannot be recommended for a field laboratory. The method proposed by Sandell and Kolthoff (1937), based on the catalytic reduction of Ce(IV) by As(III) in presence of iodide, was examined for this purpose. Rodriguez and Purdue (1969) have carried out a detailed study of the factors such as the concentrations of these two reagents, their ratio, temperature and the rate of reaction. Dubravic (1955) arrested the reaction after a fixed time interval by adding Fe(II) solution which reduces the remaining Ce(IV) to Ce(III) producing an equivalent amount of Fe(III). The absorbance of Fe(III)-CNS complex is then correlated with the iodide concentration in the system.

The presence of significant amounts of chloride in natural waters of varying salinity imposed a serious limitation on the application of this method for the determination of iodide (Dubravic 1955; Navada *et al* 1983). This paper describes an anion exchange separation step for eliminating this interference. Further, conditions have been standardized so that the method can be readily adapted in a field laboratory.

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2. Experimental

2.1 Reagents

Standard iodide solution: 0.3615 g of AnalaR grade KI was dissolved in deionised water and made up to 200 ml to get a stock solution of 1.382 mg I per ml. This solution is suitably diluted to get the working solution of 100 ng I per ml.

As(III) solution, 0.2 M: 9.98 g of arsenious oxide was dissolved in dil NaOH, acidified with H₂SO₄ and made up to 500 ml.

Ce(IV) solution, 0.01 M: 4.043 g ceric ammonium sulphate, tetrahydrate, was dissolved in water containing 90 ml of 1:1 H₂SO₄ and made up to 1 l.

Ferrous ammonium sulphate solution, 1.5% w/w.

Ammonium thiocyanate solution, 4% w/w.

Sulphuric acid, 1:1.

Ammonium nitrate solution, 0.2 M and 2 M.

Tulsion A-27 (Gel) anion exchanger, -50 + 100 mesh, in NO₃ form.

All dilutions were carried out with deionised water.

A Shimadzu UV-210A double beam spectrophotometer was used for measuring the absorbance of Ce(IV) at regular intervals and a Beckman model DU spectrophotometer for measuring the absorbance of the Fe(III)-CNS complex.

In order to demonstrate the validity of the experimental conditions, it was necessary to establish the proportionality of the rate constant with the decrease of the concentration of Ce(IV) which follows the first order (Rodriguez and Purdue 1969) and the concentration of iodide which remains unchanged during the reaction (Truesdale and Smith 1975). Expressing mathematically,

$$\begin{aligned} -d[\text{Ce(IV)}]/dt &= k \cdot [\text{Ce(IV)}] \\ &= k' \cdot [\text{Ce(IV)}] \cdot [\text{I}], \end{aligned}$$

where k is the first-order rate constant and is proportional to the concentration of iodide, i.e., $k = k'[\text{I}]$.

To a series of 10 ml volumetric flasks, containing 0.5 ml of 1:1 H₂SO₄ and 0.5 ml of As(III) solution, 0 to 80 ng of iodide were added and the volume kept at 8 ml by adding the requisite amount of deionised water. The flasks were kept in a constant temperature bath (a fish pond with an arrangement to keep the flasks in a stable position) for about 15 minutes. Then exactly 0.5 ml of Ce(IV) solution was added to the first flask, simultaneously a stop-watch was started. The flask was made up and the absorbance measured at 360 nm using 1 cm cells, at regular intervals of 2 to 3 minutes. The experiment was repeated for the other flasks. From the plot of log(absorbance) vs. the duration of the reaction, the half-time, T , for each concentration of iodide was found out. The rate constant k , given by $0.693/T$, is then computed and plotted against iodide concentration. The curve, figure 1, is linear and passes through the origin, in agreement with the equations proposed by Rodriguez and Purdue (1969) and Truesdale and Smith (1975).

This method involves the measurement of Ce(IV) concentration over a period of time and obtaining the rate constant graphically. It would be simpler, especially for routine analysis, to make a measurement of Ce(IV) after a fixed time-interval and

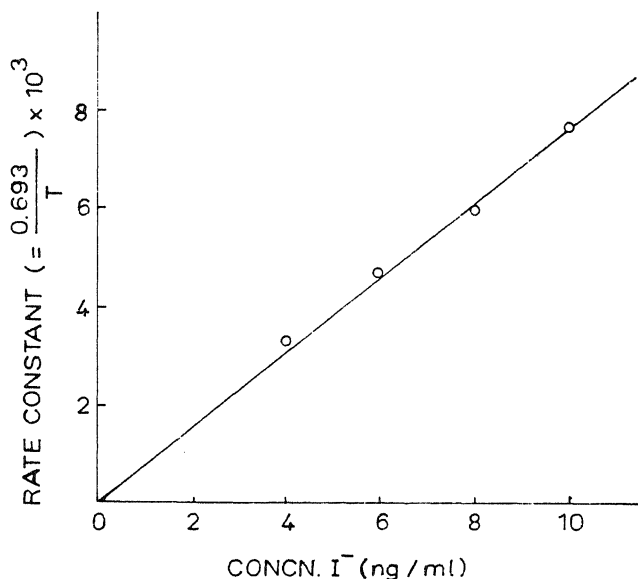


Figure 1. Relation between rate-constant and iodide concentration.

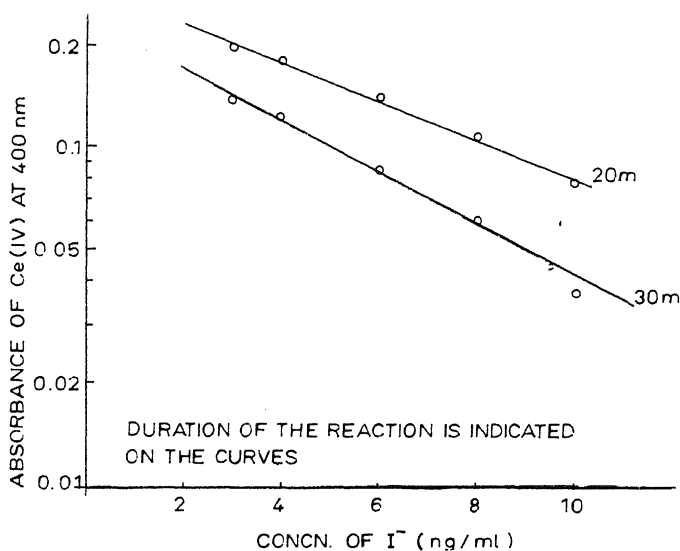


Figure 2. Variation of absorbance of Ce(IV) with iodide concentration.

correlate this with the iodide concentration. This is shown for two intervals of 20 and 30 minutes in figure 2.

A further improvement in this method has been suggested by Dubravic (1955). This is to arrest the reaction after a chosen time interval by addition of excess of Fe(II) solution. This converts the remaining Ce(IV) in the system to an equivalent amount of Fe(III) which can be conveniently estimated by the absorbance of the Fe(III)-thiocyanate complex at 460 nm. We found that this method, in addition to being convenient, is also more sensitive. The time interval is chosen such that the

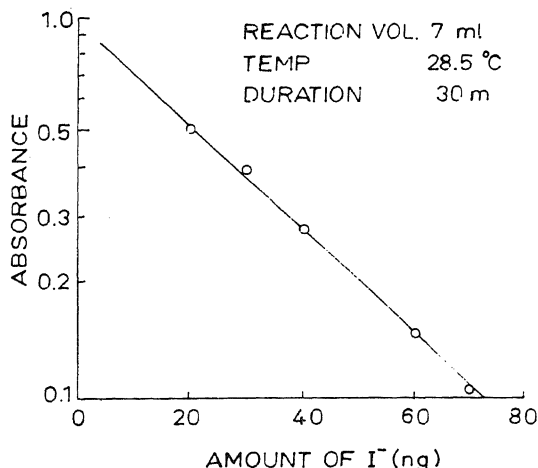


Figure 3. Calibration curve for iodide using the arresting method.

yellow colour of Ce(IV) just fades. This will be smaller when the iodide concentration is higher and vice versa. The feasibility of using this method in the present case was studied by repeating the experiment, keeping the reaction volume at 7 ml. To a series of flasks containing the reagents as before, 0.5 ml of Ce(IV) solution was added at intervals of 0.5 min. At the end of 30 minutes, the reaction was arrested by adding 0.5 ml of Fe(II) solution in the same order at intervals of 0.5 minute. The colour was then developed by the addition of 0.5 ml of thiocyanate solution and the absorbance of the complex measured using 1 cm cells, at 460 nm, after 15 minutes. In this manner, a number of samples could be handled at the same time and analyses carried out conveniently.

Figure 3 gives the calibration curve obtained.

3. Preseparation

The presence of chloride in the saline water samples poses a major interference in the analysis by the catalytic method. Thus, the elimination of chloride prior to the determination is required. In our earlier paper, we reported the separation of nanogram amounts of iodide from 1 g of sodium chloride on a column containing 300 mg of Deacidite FF anion exchanger in the NO_3 form. In this step, the chloride content was reduced from 600 mg to less than 0.3 mg in the resin phase, while iodide was retained. The same procedure was followed in the present study. Iodide was recovered subsequently by elution from the column.

Preliminary experiments on 300 mg of Deacidite FF resin indicated that 2 M ammonium nitrate solution eluted nearly 90% of the iodide within a volume of 10 ml, the remaining having been lost in the separation step. Experiments were carried out using 1 g of the indigenously available Tulsion A-27(Gel) anion exchanger in the NO_3 -form. The procedure consisted of loading the saline water sample (1 ml), removal of chloride and bromide with 10 ml of 0.2 M ammonium nitrate, followed by elution of iodide with 2 M ammonium nitrate (15 ml). The

Table 1. Elution of iodide from the column.

Weight of resin	: 1 g (NO ₃ ⁻ form)
Loading volume	: 5 ml
Volume per fraction of eluate	: 5 ml
Elution of Cl ⁻ and Br ⁻	: 5 ml 0.2 M NH ₄ NO ₃
Elution of iodide	: 5 ml fractions of 2 M NH ₄ NO ₃

Iodide loaded (ng)	Iodide eluted in each fraction (%)					Total (%)
	1	2	3	4	5	
200	7.6	71.5	18.1	2.9	0.7	100.8
500	7.7	71.2	16.2	3.8	0.9	99.8
1000	2.6	83.9	9.8	1.1	0.4	97.8

Table 2. Effect of chloride ion.

Iodide taken (ng)	Absorbance of Fe-CNS complex at 460 nm				
	No Cl ⁻	1 mg Cl ⁻	2 mg Cl ⁻	3 mg Cl ⁻	4 mg Cl ⁻
0	0.750	0.734	0.742	0.750	—
5	0.640	0.631	0.618	0.595	0.551
10	0.533	0.489	0.450	0.470	0.450
15	0.353	0.353	0.345	0.331	0.334
20	0.313	0.310	0.290	0.261	0.261

Initial Ce(IV) concentration	: 1.4×10^{-4} M
Initial As(III) concentration	: 7.0×10^{-5} M
Temperature	: 26.5°C
Duration of the reaction	: 40 m

Table 3. Effect of nitrate ion.

Iodide taken (ng)	Absorbance of Fe-CNS complex	
	No NH ₄ NO ₃	0.5 M NH ₄ NO ₃
10	0.418	0.382
15	0.285	0.266
20	0.199	0.191
25	0.149	0.153

Temperature: 28.5°C

Duration of reaction: 60 m

recovery by this method for varying amounts of iodide labelled with I-131 tracer is given in table 1.

Next, the effect of chloride and ammonium nitrate on the determination by the arresting method was studied. Tables 2 and 3 give the results.

4. Results and discussion

The presence of upto 2 mg of chloride in the aliquot used for the determination does not affect the measured value more than 10%. Navada *et al* (1983) have found no interference from 200 ppm chloride. In view of the decontamination factor of nearly 2000 by this method, even samples containing tens of milligrams of chloride per ml can be analysed. Similarly, measurements in the presence of 0.5 M ammonium nitrate also indicate no appreciable effect on the measured value. This concentration of NH_4NO_3 corresponds to what is expected in the solution used for the measurement, after the elution step.

A few water samples from the coastal areas of Tamil Nadu, containing 0.2 to 30 mg of chloride per ml, were analysed for iodide by the present method. The results are given in table 4. The first four samples containing 20–50 ppb of iodide were also analysed by neutron activation (Krishnamoorthy and Iyer 1983). The agreement between the results is satisfactory, considering the low levels of concentrations. It further establishes the validity of the separation method, since as much as 28 mg of chloride per ml, present in the sample, does not give a positive interference. In tap water, 0.5 ppb levels of iodide have been determined, and the values compare well with those by the neutron activation technique.

5. Conclusion

The method of pre-separation and its determination by the catalytic method can be readily adopted in a field laboratory for samples containing 0.5 to 50 ppb of iodide and upto 30 mg of chloride per ml. As reported earlier, the method can be applied for the analysis of common salt also. The chemicals and the anion exchanger are indigenously available and the analysis involves only three steps, namely, (i) anion

Table 4. Analysis of water samples.

Code nos.	Chloride (mg/ml)	Conc. of Iodide in ppb	
		by this method	by N.A.A
<i>Saline waters-I</i>			
171	0.28	28	23
172	8.15	39	56
173	27.8	51	71
175	1.1	37	45
<i>Saline waters-II</i>			
33	n.a.	13	
52	n.a.	13	
53	n.a.	7	
75	n.a.	9	
<i>Tap water</i>			
1	—	0.5	0.5
2	—	1.2	0.8

n.a.: not available.

exchange, separation and elution, (ii) catalytic reaction and (iii) absorbance measurement.

The overall precision of the procedure by the arresting method was found to be 6% which compares well with the neutron activation analysis.

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Synthesis, characterisation and chemical reactivity of some new dioxouranium(VI) complexes of 2-aminobenzoylhydrazone of butane-2,3-dione

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Abstract. A new series of dioxouranium(VI) complexes of a potential ONNO tetradentate donor 2-aminobenzoylhydrazone of butane-2,3-dione (L_1H_2) have been synthesized. At pH 2.5-4.0, the donor (L_1H_2) reacts in the keto form and complexes of the type $[UO_2(L_1H_2)(X)_2]$ ($X^- = Cl^-, Br^-, NO_3^-, NCS^-, ClO_4^-, CH_3COO^-, \frac{1}{2}SO_4^{2-}$) are obtained. At higher pH (6.5-7), the complex of the enol form having the formula $[UO_2(L_1)(H_2O)]$ has been isolated. On reaction with a monodentate lewis base (B), both types of complexes yield adducts of the type $[UO_2(L_1)(B)]$. All these complexes have been characterised adequately by elemental analyses and other standard physicochemical techniques. Location of the bonding sites of the donor molecule around the uranyl ion, status of the uranium-oxygen bond and the probable structure of the complexes have also been discussed.

Keywords. Synthesis; chemical reactivity; dioxouranium(VI) complexes; 2-aminobenzoylhydrazone of butane-2,3-dione.

1. Introduction

Ligational behaviour of acid hydrazones of alpha-ketooximes towards several first row transition metal ions have been studied in detail (Mostafa *et al* 1980, 1983; Ghosh *et al* 1984, 1985; Ghosh and Maiti 1987). But the coordination ability of the acid hydrazones of alpha-diketones acting as tetradentate donors towards oxometal cations have not been adequately explored. The present work reports the synthesis of a tetradentate ONNO donor from *o*-aminobenzoylhydrazide and diacetyl and its ligational behaviour towards the dioxouranium(VI) cation. A series of dioxouranium(VI) complexes of both keto and enol forms of the donor have been isolated and characterised. These complexes have also been prepared by reacting diacetyl with the corresponding uranyl complexes of *o*-aminobenzoyl hydrazide. Reactivity of these complexes towards some monodentate lewis bases (like pyridine, methylamine etc.) have been explored. The status of the uranium-oxygen multiple bond have also been discussed.

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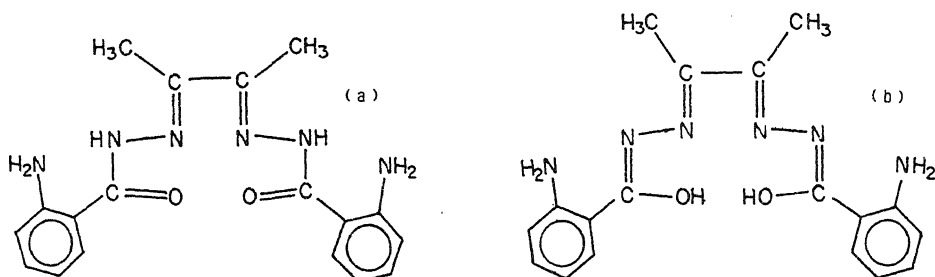


Figure 1. Keto (a) and enol (b) forms of the donor.

2. Experimental

2.1 Preparation of the Schiff base (L_1H_2)

o-Aminobenzoyl hydrazide was prepared by refluxing methyl anthranilate (0.01 mol) with hydrazine hydrate (99.9%, 0.0125 mol) in the presence of a few ml of dry ethanol. The Schiff base (L_1H_2) was obtained by the reaction of diacetyl on *o*-aminobenzoylhydrazide in 1:2 molar ratio in ethanol medium at room temperature in the presence of 2–3 drops of conc. HCl. The desired compound was isolated as a yellow powder. It is sparingly soluble in methanol and ethanol and highly soluble in DMF and DMSO. The melting point of this compound is 276°C. Carbon, hydrogen and nitrogen analysis of this compound corresponds very well with the molecular formula $C_{18}H_{20}N_6O_2$. The donor (L_1H_2) can exist both in the keto and the enol forms as shown in figures 1a and b, respectively.

2.2 Syntheses of the complexes

The $[UO_2(L_1H_2)(X)_2]$ -type complexes ($X^- = Cl^-, Br^-, NO_3^-, NCS^-, ClO_4^-, CH_3COO^-, \frac{1}{2}SO_4^{2-}$) having the keto form of the donor were obtained by adding an ethanolic solution of the hydrated uranyl salt to a well-stirred alcoholic suspension of the ligand in 1.25:1 molar ratio. An orange-yellow to red coloured compound gradually separated out (pH $\approx$ 2.5–4.0). It was filtered, washed with alcohol and finally dried over fused $CaCl_2$.

The above keto compounds were also obtained by stirring an ethanolic suspension of the corresponding uranyl complexes of *o*-aminobenzoylhydrazide with diacetyl in 1:1.25 molar ratio for 1–2 hr at room temperature.

The complex $[UO_2(L_1)(H_2O)]$ containing the bianionic enolate ligand was prepared by raising the pH of a suspension of any of the $[UO_2(L_1H_2)(X)_2]$ -type complexes to $\approx$ 7–7.5 in rectified spirit by the careful addition of alcoholic NaOH solution and stirring the mixture for $\approx$ 8–10 hr. The resulting orange-red compound was filtered, washed with a little ethanol and then thoroughly with water. It was dried over fused $CaCl_2$.

Preparation of $[UO_2(L_1)(B)]$ -type complexes ($B = Py, CH_3NH_2$ etc.): The pyridine adduct $[UO_2(L_1)(Py)]$ was obtained by heating under reflux (or simply stirring at room temperature) an ethanolic suspension of either the enol or a keto compound with a little excess of pyridine for $\approx$ 2 hr and evaporating the orange-red solution to a small volume at room temperature. An orange-red

Table 1. Analytical and physical data for the uranyl complexes.

Compound	Colour	Found (calcd.) %	C	H	Anion	Λ_M ($\Omega\text{cm}^{-1}\text{cm}^2$ mol^{-1})	$R_{U-O(O)}$ ($\text{\AA}^\circ$)	$F_{U-O(O)}$ (milli- dynes/ $\text{\AA}^\circ$)
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{SO}_4)]\cdot\text{H}_2\text{O}$	Orange-red	32.22 (32.34)	11.20 (11.41)	28.32 (29.35)	3.20 (2.99)	13.20 (13.04)	1.753	6.163
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{NO}_3)_2]$	Red	31.68 (31.90)	14.60 (15.01)	28.05 (28.95)	2.80 (2.68)	—	1.750	6.215
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{CH}_3\text{COO})_2]$	Orange-yellow	32.00 (32.16)	11.17 (11.35)	35.04 (35.67)	3.69 (3.51)	—	1.764	5.98
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{ClO}_4)_2]$	Orange	28.82 (28.99)	10.06 (10.23)	25.55 (26.31)	2.24 (2.44)	24.15 (24.24)	1.747	6.267
$[\text{UO}_2(\text{L}_1\text{H}_2)\text{Cl}_2]$	Orange-red	34.04 (34.34)	12.30 (12.12)	30.25 (31.17)	3.00 (2.88)	10.00 (10.24)	1.759	6.063
$[\text{UO}_2(\text{L}_1\text{H}_2)\text{Br}_2]$	Red	30.33 (30.43)	10.47 (10.74)	26.57 (27.62)	2.78 (2.55)	20.08 (20.46)	1.756	6.113
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{NCS})_2]$	Reddish brown	32.42 (32.25)	14.87 (15.17)	33.10 (32.52)	2.90 (2.71)	—	1.763	5.996
$[\text{UO}_2(\text{L}_1)(\text{H}_2\text{O})]$	Orange-red	37.20 (37.30)	13.00 (13.16)	32.80 (33.85)	2.97 (3.13)	—	1.764	5.980
$[\text{UO}_2(\text{L}_1)(\text{Py})]$	Orange-red	34.01 (34.05)	14.18 (14.02)	38.55 (39.48)	3.48 (3.29)	—	1.767	5.931
$[\text{UO}_2(\text{L}_1)(\text{MeNH}_2)]$	Yellow	36.28 (36.56)	14.80 (15.05)	34.40 (35.02)	3.37 (3.53)	—	1.769	5.899
L_1H_2	Light-yellow	—	23.75 (23.86)	61.45 (61.36)	5.28 (5.68)	—	—	—

Table 2. Some characteristic IR spectral bands of the uranyl complexes* (cm^{-1}).

Compound	$\nu(\text{NH}_2)$ (<i>asym</i> and <i>sym</i>)	$\nu(\text{C}=\text{O})$ <i>amide I</i>	$\nu(\text{C}=\text{N})$ <i>azomethine</i>	$\nu(\text{CN}) + \delta(\text{NH})$ <i>amide II</i>	$\nu_3(\text{UO}_2)$ (<i>asym</i>)
L_1H_2	3480 <i>s</i> 3380 <i>s</i>	1640 <i>s</i>	1608 <i>s</i>	1550 <i>s</i>	
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{SO}_4)]\text{H}_2\text{O}$	3480–3420 <i>s</i> , <i>br</i> 3380–3330 <i>s</i> , <i>br</i>	1620 <i>s</i>	1585 <i>s</i>	1545 <i>s</i>	920 <i>s</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{NO}_3)_2]$	3480 <i>s</i> 3380 <i>s</i>	1615 <i>s</i>	1580 <i>s</i>	1540 <i>s</i>	925 <i>s</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{CH}_3\text{COO})_2]$	3480 <i>s</i> 3375 <i>s</i>	1620 <i>s</i>	1580 <i>s</i>	1535 <i>m</i>	903 <i>s</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{ClO}_4)_2]$	3480 <i>s</i> 3380 <i>s</i>	1612 <i>s</i>	1580 <i>s</i>	1540 <i>s</i>	930 <i>s</i> , <i>br</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)\text{Cl}_2]$	3480 <i>s</i> 3375 <i>s</i>	1610 <i>s</i>	1580 <i>s</i>	1535 <i>s</i>	910 <i>s</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)\text{Br}_2]$	3480 <i>s</i> 3380 <i>s</i>	1610 <i>s</i>	1585 <i>s</i>	1540 <i>m</i>	915 <i>s</i>
$[\text{UO}_2(\text{L}_1\text{H}_2)(\text{NCS})_2]$	3480 <i>s</i> 3380 <i>s</i>	1615 <i>s</i>	1585 <i>s</i>	1540 <i>m</i>	905 <i>s</i>
$[\text{UO}_2(\text{L}_1)(\text{H}_2\text{O})]$	3475 <i>s</i> 3375 <i>s</i>	—	1585 <i>s</i>	—	903 <i>s</i>
$[\text{UO}_2(\text{L}_1)(\text{Py})]$	3480 <i>s</i> 3380 <i>s</i>	—	1585 <i>s</i>	—	898 <i>s</i>
$[\text{UO}_2(\text{L}_1)(\text{MeNH}_2)]$	3465 <i>s</i> 3300 <i>s</i>	—	1580 <i>s</i>	—	895 <i>s</i>

* *s* = strong, *m* = medium, *br* = broad

compound slowly separated out. It was filtered and washed with ethanol and dried over fused CaCl_2 . The methyl amine compound was obtained by the above method, the pH of the mixture being adjusted to $\approx 7\text{--}7.5$ by the addition of dry alcoholic methyl amine solution. It is to be noted that we could not isolate eight coordinated complexes of the formula $[\text{UO}_2(\text{L}_1)(\text{B})_2]$ and $[\text{UO}_2(\text{L}_1)(\text{B--B})]$, where B--B = a bidentate lewis base like α , α' -dipyridyl or *o*-phenanthroline.

2.3 Analyses of the complexes

Uranium was estimated by the oxime method (Vogel 1961). Carbon, hydrogen and nitrogen were determined by the Perkin Elmer 240C Elemental Analyser. The anions were analysed by standard analytical procedures (Vogel 1961).

2.4 Physical measurements

Magnetic susceptibilities of the compounds were recorded by a EG & G PAR Vibrating Sample Magnetometer (model 155). UV spectra was recorded in DMSO solvent using a Pye-Unicam SP8-150 UV-VIS spectrophotometer. IR spectra were taken in KBr on a Perkin Elmer 783 IR spectrophotometer. Conductance measurements were performed in DMSO with the help of a Philips conductivity

bridge (PR 9500). The chemical formulae of the complexes together with their analytical data, colour, molar conductance value (Λ_M), uranium-oxygen multiple bond length $R_{U-O(1)}$, and force constant $F_{U-O(1)}$, are included in table 1. Important infrared spectral bands are presented in table 2.

3. Results and discussion

The colour of the dioxouranium(VI) complexes varied from yellow to red. The compounds of the type $[UO_2(L_1H_2)(X)_2]$ are moderately soluble (except the sulphate and the acetate compound) in methanol, ethanol, acetone and sparingly soluble in benzene, chloroform and carbon tetrachloride. All of them are highly soluble in DMSO and DMF.

As is expected for d^0 systems, all the dioxouranium(VI) complexes are diamagnetic.

All the uranyl complexes behave as non-electrolytes in solution. The non-ionic nature of the keto compounds $[UO_2(L_1H_2)(X)_2]$ indicates the existence of coordinated anions in all these complexes which is corroborated by the relevant IR data.

3.1 Infrared spectra

Presence of the $\nu(NH_2)$ modes of the aromatic ring $-NH_2$ group at 3480 cm^{-1} (ν_{as}) and 3380 cm^{-1} (ν_s) (Bellamy 1975) and disappearance of the $\nu(NH_2)$ modes of the hydrazinic $-NH_2$ group in the IR spectrum of the free donor (L_1H_2) clearly indicates that the Schiff base formation has taken place exclusively from the hydrazinic $-NH_2$ group of *o*-aminobenzoyl hydrazide leaving the aromatic ring $-NH_2$ group free. In all the complexes the position of $\nu(NH_2)$ of the free donor remains almost unaltered (table 2) indicating the non-participation of the ring $-NH_2$ group in coordination to the metal ion. The presence of a free aromatic $-NH_2$ group in the L_1H_2 molecule is confirmed through the diazo reaction. The amide I band ($\nu_{C=O}$) located at 1640 cm^{-1} (Bellamy 1975) and the $\nu(C=N)$ at 1608 cm^{-1} in the IR spectrum of the free donor are shifted to lower frequencies in all the complexes having the keto form of the donor. This clearly indicates that the donor L_1H_2 coordinates to the UO_2^{2+} acceptor centre through its amide carbonyl oxygen and the azomethine nitrogen (Percy and Thornton 1971), respectively.

In the complexes obtained at higher pH in solution, the amide I band disappears completely. This clearly demonstrates that at higher pH, the donor enolises and binds the metal ion subsequently via two deprotonated enolate oxygens and two azomethine nitrogens. A new band is found to appear at $\sim 1615\text{ cm}^{-1}$ indicating the generation of a new $>C=N$ bond due to the enolisation of the $-NH-C=O$ group.

Characteristic IR bands of the complexes containing nitrate, perchlorate, acetate, indicate the presence of these anions in the monocoordinated fashion (Nakamoto 1978). Relevant IR spectra also indicate that the CNS^- ion is coordinated to the metal ion through the nitrogen atom. The presence of coordinated Cl^- and Br^- ions are substantiated by the nonelectrolyte nature of the corresponding complexes. The characteristic features of the IR spectrum of the

compound $[\text{UO}_2(\text{L}_1\text{H}_2)(\text{SO}_4)]\text{H}_2\text{O}$ clearly show that the SO_4^{2-} ion is coordinated in a bidentate manner. In the spectrum of the pyridine adduct, the in-plane ring deformation mode of pyridine (at 604 cm^{-1}) is shifted to a higher frequency (640 cm^{-1}), implying coordination from the pyridine nitrogen (Gill *et al* 1961). Specific bands of the coordinated water molecule are also observed in the complex $[\text{UO}_2(\text{L}_1)(\text{H}_2\text{O})]$ which contains H_2O in the inner sphere.

In view of the fact that the UO_2^{2+} moiety existing in most dioxouranium(VI) complexes is crystallographically linear (Hsieh *et al* 1975; Cattalini *et al* 1971), it is reasonable to expect the occurrence of a linear UO_2 moiety in the complexes described herein. The IR spectra of the uranyl complexes exhibit an intense absorption in the $890\text{--}930\text{ cm}^{-1}$ region attributable to the ν_3 or ν_{as} (UO_2) mode (Jones 1958). The ν_s (UO_2) expected in the region $800\text{--}900\text{ cm}^{-1}$ is generally very weak as reported earlier (Hsieh *et al* 1975). In the present study, the position of the $\nu_s(\text{UO}_2)$ could not be established unequivocally because of the presence of several ligand absorptions in the same region.

3.2 $\text{U}-\text{O}_{(1)}$ bond length and force constant

Infrared spectroscopy has been utilised for the evaluation of the $\text{U}-\text{O}$ bond lengths (Veal *et al* 1975) of the dioxouranium(VI) complexes. The two axial or uranyl oxygen atoms form the primary $\text{U}-\text{O}_{(1)}$ bonds and these $\text{U}-\text{O}$ bond lengths (R) vary as a function of the other donor atoms or groups present around the uranyl moiety. From the IR data of our compounds the primary $\text{U}-\text{O}_{(1)}$ bond distance has been calculated using a previously reported procedure (Veal *et al* 1975) and the results are presented in table 1. The force constant $F_{\text{U}-\text{O}_{(1)}}$ is also calculated by the method of McGlynn (McGlynn and Smith 1961) and are also included in table 1. Excepting the case of the sulphate compound, the shift of $\nu_{as}(\text{UO}_2)$ with the change of the coordinated anion in the equatorial plane is fairly consistent with the position of the anions in the spectrochemical series (Cotton and Wilkinson 1980). The stronger the donor character of the anion, the greater is the shift of the $\nu_{as}(\text{UO}_2)$ mode towards lower frequencies. This is also reflected in the variation of the $F_{\text{U}-\text{O}_{(1)}}$ in the reverse direction. In its enol form the donor is a stronger σ -donor than its keto counterpart because of the involvement of the two negatively charged enolate oxygens in coordination to the UO_2^{2+} moiety in place of the two neutral amide carbonyl oxygens. It is also quite expected that the $\nu_{as}(\text{UO}_2)$ band will be shifted towards lower frequency when a stronger σ -donor replaces a weaker donor in the equatorial plane. In practice, the $\nu_{as}(\text{UO}_2)$ located at 903 cm^{-1} for the compound $[\text{UO}_2(\text{L}_1)(\text{H}_2\text{O})]$ is shifted to lower wave number when the H_2O molecule is replaced by pyridine or CH_3NH_2 in accordance with the position of H_2O , Py or CH_3NH_2 in the spectrochemical series.

3.3 Electronic spectra

The UV spectra of the uranyl complexes exhibit a strong band in the $21,000\text{--}22,500\text{ cm}^{-1}$ region (Shallaby *et al* 1984). This is assigned to the uranyl absorption as ${}^3\pi_u \leftarrow {}^1E_g^+$ for the first excited state (McGlynn and Smith 1961). However, it has not been possible to assign several other bands observed beyond $25,000\text{ cm}^{-1}$ in the spectra of the complexes.

3.4 Structure and reactivity of the complexes

IR and conductivity data indicates that in all the $[UO_2(L_1H_2)(X)_2]$ -type of complexes the anions are coordinated to the dioxouranium(VI) ion. Hence, it appears that the uranyl complexes of the keto form are 8-coordinated with the ONNO donor sites of the tetradentate donor spanning four adjacent positions while the two anions occupy the remaining two adjacent positions in the hexagonal equatorial plane. The two uranyl oxygens are bonded axially (figure 2). This is supported by the fact that the two anions (X) of the $[UO_2(L_1H_2)(X)_2]$ -type complex are replaced by one oxalate ion even at room temperature when the complex is treated with alcoholic oxalic acid solution. The product is a yellow compound of formula $[UO_2(L_1H_2)(C_2O_4)]$. Conductivity data indicate that it is a nonelectrolyte and the IR spectrum of this compound shows that the oxalate ion is attached to the dioxouranium(VI) species in a bicoordinated fashion. Therefore, from the above considerations, probable structure of the complexes of the keto form of the donor may be written as in figure 2. The complex of the enol form $[UO_2(L_1)(H_2O)]$ appears to be a seven-coordinated species. In this complex, of the five donor points present in the equatorial plane, four points are occupied by the enolised donor while one water molecule sits in the fifth position. Reactions of $[UO_2(L_1)(H_2O)]$ with excess monodentate nitrogen donors such as pyridine, picolines, methylamine etc. always led to the formation of the complex $[UO_2(L_1)(B)]$ and hence supports the seven coordinated structure (Bandoli *et al* 1972; Cattalini *et al* 1972). The complex $[UO_2(L_1)(H_2O)]$ exhibits the loss of only one water molecule at a quite high temperature range of 155–210°C. This indicates that the only water molecule present in the complex is coordinated to the uranyl moiety. The anhydrous compound thus obtained again forms $[UO_2(L_1)(B)]$ on treatment with the base (B). These two observations support the seven coordinated structure of $[UO_2(L_1)(H_2O)]$ and $[UO_2(L_1)(B)]$. Hence, the structure of the complex $[UO_2(L_1)(H_2O)]$ may be represented as in figure 3. The structure of its reaction products with (B) can easily be visualized by replacing the water molecule in figure 3 by (B).

It appears that the compound $[UO_2(L_1)(H_2O)]$ shows a strong preference towards seven-coordination. As expected from the hard acceptor UO_2^{2+} , the

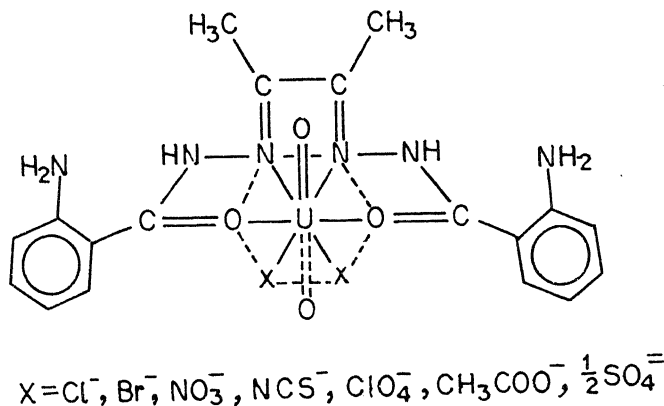


Figure 2. Donor environment around $U^{VI}O_2$ in $[UO_2(L_1H_2)(X)_2]$ -type complexes.

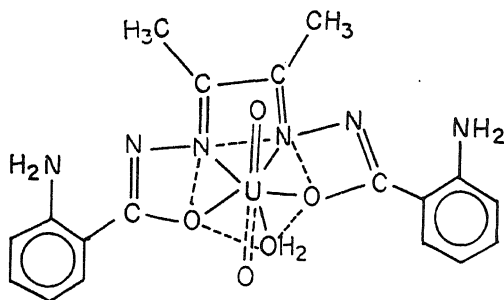


Figure 3. Donor environment around $\text{U}^{\text{VI}}\text{O}_2$ in $[\text{UO}_2(\text{L}_1)(\text{H}_2\text{O})]$.

compound $[\text{UO}_2(\text{L}_1)(\text{H}_2\text{O})]$ did not react with the soft donors (Cattalini *et al* 1972; Pearson 1963, 1966) like PPh_3 , thiophen, thioethers and mercaptans. Triphenyl phosphine failed to effect oxygen abstraction from the UO_2^{2+} moiety in any of the reported complexes even after prolonged heating under reflux.

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Copper(II), nickel(II), palladium(II) and iron(III) complexes of 2-(3-phthalhydrazidylazo)-1,3-diketones

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Abstract. Neutral complexes of three phthalhydrazidylazo-1,3-diketones [phthalhydrazidylazo-acetylacetone (H_2PAA), -benzoylacetone (H_2PBA) and -dibenzoylmethane (H_2PDM)] with Cu(II), Ni(II), Pd(II) and Fe(III) have been synthesised and characterized on the basis of their analytical data, magnetic moment, molar conductance and IR and 1H NMR spectral data. Dibasic tridentate coordination of the ligands is brought out by the above spectral data. Half-wave potentials and far IR spectral data of the Cu(II) complexes indicate that the H_2PAA complex is the most stable. Mössbauer spectra of the Fe(III) complexes reveal that delocalisation of the metal d electrons with the chelate ring decreases with increasing capability of the pendant groups of the ring for cross conjugation.

Keywords. Phthalhydrazidylazo-1,3-diketones; transition metal complexes; IR spectra; NMR spectra; Mössbauer spectra; stability of complexes.

1. Introduction

Extensive literature is available on metal chelates of *o*, *o'*-disubstituted diarylazo compounds, which have significant application as stable dyestuffs and as analytical reagents (Venkataraman 1952; Price 1970). However, very few reports exist on metal complexes of azo dyes formed from heterocyclic amines via diazotization, and coupling with the reactive methylene group of β -diketones. Details of the synthesis and characterization of Cu(II), Ni(II), Pd(II) and Fe(III) complexes of three phthalhydrazidylazo-1,3-diketones prepared from 3-aminophthalhydrazide (the chemiluminescent organic compound well-known by its trivial name 'luminol') are brought out in this paper, the 1,3-diketones used being acetylacetone, benzoylacetone and dibenzoylmethane.

2. Experimental

2.1 Preparation of 2-(3-phthalhydrazidylazo)-1,3-diketones

Phthalhydrazidylazoacetylacetone (H_2PAA), phthalhydrazidylazo-benzoylacetone (H_2PBA) and phthalhydrazidylazodibenzoylmethane (H_2PDM) were prepared as reported earlier (Thankarajan *et al* 1986).

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2.2 Preparation of metal complexes

Copper(II) complexes were prepared by adding an aqueous solution (15 ml) of the metal(II) acetate (2.5 mmol) to a stirred ethanolic solution (100 ml) of the ligand (2.5 mmol) maintained at $\sim 60^\circ\text{C}$. After refluxing the mixture for 2 hr, the precipitated complex was filtered, washed successively with water, ethanol and diethyl ether, and then dried in vacuum. For preparing palladium(II) complexes, palladium(II) chloride (0.215 g, 1 mmol) dissolved in acetone (25 ml) was added to a hot and stirred solution (50 ml) of the ligand (1 mmol). The mixture was refluxed for about 1 hr, the precipitated complex filtered, washed with ethanol, and recrystallised from hot ethanol.

Iron(III) complexes were prepared by mixing an ethanolic solution (10 ml) of iron(III) chloride hexahydrate (0.135 g, 5 mmol) with a hot and stirred solution of the ligand (5 mmol) in ethanol (50 ml). The deep brown precipitate formed on adding sodium acetate (0.1 g) was filtered, washed with very dilute acetic acid and ethanol, and then dried in vacuum.

2.3 Physical measurements

Molar conductance was measured at $28 \pm 0.2^\circ\text{C}$ in ethanol (10^{-3} M) using a Toshniwal conductivity bridge. Magnetic susceptibilities were determined at room temperature on a Gouy type magnetic balance. Infrared spectra (Nujol mull and KBr disc) were recorded on a Perkin-Elmer 257 spectrometer, and far IR spectra (CsI disc) on a polytech FIR spectrometer. ^1H NMR spectra ($\text{DMSO}-d_6$) were obtained from a Varian XL-100 FT NMR spectrometer. For recording Mössbauer spectra (natural iron as reference), a constant acceleration Mössbauer spectrometer ECIL MBS 35 coupled to a multichannel analyser NCA 38 was used. Polarograms were recorded in aqueous pyridine (50% v/v) using KNO_3 as supporting electrolyte on an Elico pen recording polarograph. Carbon, hydrogen and nitrogen percentages reported are by microanalyses, and metal contents by standard gravimetric procedures.

3. Results and discussion

All complexes behave as non-electrolytes (specific conductance $< 10 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$), and do not contain the anion of the metal salt used for preparing them. Nickel(II) and palladium(II) complexes are diamagnetic, while copper(II) complexes show normal magnetic moments of 1.78–1.82 B.M. Magnetic moment of the iron(III) complexes are in the high spin range of 5.90–5.95 B.M. Based on elemental analysis, molar conductance and magnetic moment data the complexes are represented as in table 1.

3.1 IR spectra

Infrared and ^1H NMR spectral data indicate that the three phthalhydrazidylazo- β -diketones exist as hydrogen bonded hydrazoneenol, as in the structure I (Thankarajan *et al* 1986). Thus, while the IR spectrum of H_2PAA showed a strong band at 1672 cm^{-1} for free acetyl carbonyl, spectra of H_2PBA and H_2PDM showed

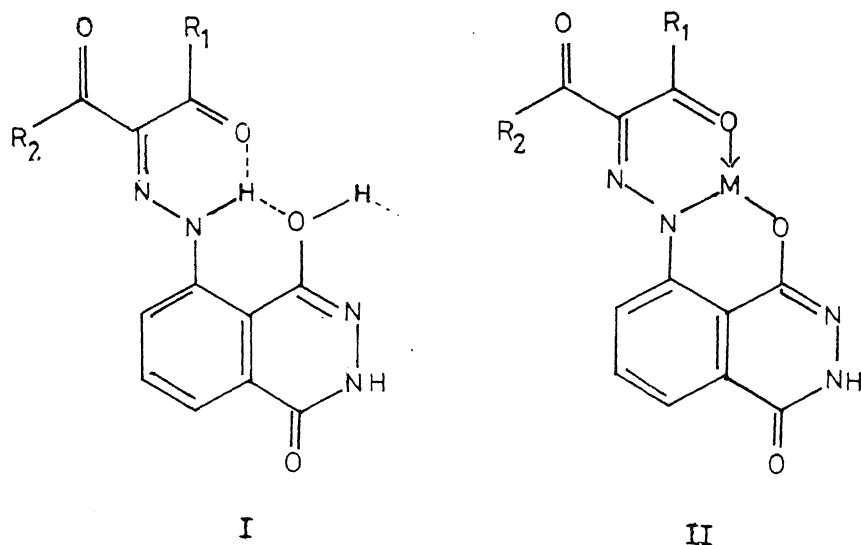
Table 1. Analytical data and other details about the metal complexes of 2-(3-phthalhydrazidylazo)-1,3-diketones.

Complex	Yield (%)	M.P. (°C)	μ_{eff} (B.M.)	Found (Calcd.) (%)			
				C	H	N	Metal
[Cu(PAA) (H ₂ O)]	65	a	1.82	42.01 (42.44)	2.98 (3.27)	14.86 (15.23)	17.12 (17.28)
[Cu(PBA) (H ₂ O)]	58	a	1.79	49.68 (50.28)	3.13 (3.25)	12.86 (13.03)	14.56 (14.79)
[Cu(PDM) (H ₂ O)]	55	a	1.78	55.73 (56.15)	3.09 (3.26)	11.01 (11.39)	12.78 (12.93)
[Ni(PAA) (H ₂ O)]	65	328	D	42.59 (43.01)	3.20 (3.31)	15.10 (15.44)	15.91 (16.18)
[Ni(PBA) (H ₂ O)]	50	296	D	50.13 (50.86)	3.08 (3.29)	12.93 (13.19)	13.16 (13.82)
[Ni(PDM) (H ₂ O)]	45	254	D	55.98 (56.71)	2.86 (3.29)	11.12 (11.50)	11.78 (12.06)
[Pd(PAA) (H ₂ O)]	60	350d	D	38.23 (38.80)	2.56 (2.98)	13.12 (13.65)	
[Pd(PBA) (H ₂ O)]	70	285d	D	44.86 (45.33)	2.69 (2.95)	11.33 (11.85)	
[Pd(PDM) (H ₂ O)]	75	220d	D	51.06 (51.45)	2.45 (2.98)	9.97 (10.48)	
[Fe(PAA) (OH) (H ₂ O) ₂]	62	a	5.91	39.76 (40.33)	3.78 (3.88)	13.86 (14.18)	14.00 (14.14)
[Fe(PBA) (OH) (H ₂ O) ₂]	58	a	5.93	47.88 (48.12)	3.69 (3.79)	12.15 (12.25)	12.16 (12.22)
[Fe(PDM) (OH) (H ₂ O) ₂]	56	a	5.94	53.69 (54.03)	3.58 (3.72)	10.58 (10.79)	10.83 (10.96)

a = does not melt or decompose below 350°C; d = decomposes; D = diamagnetic.

strong bands at $\sim 1660 \text{ cm}^{-1}$ for free benzoyl carbonyl. Spectra of all the three ligands showed strong bands at $\sim 1650 \text{ cm}^{-1}$ for the amide carbonyl of the phthalhydrazide moiety, and strong and broad bands at $\sim 1615 \text{ cm}^{-1}$ for the internally hydrogen-bonded carbonyl of the β -diketone moiety.

In the spectra of the metal complexes, the latter band almost disappeared, but instead, another strong band, assignable to the stretching of the coordinated carbonyl of the β -diketone moiety appeared at $\sim 1550 \text{ cm}^{-1}$ (Nakamoto 1978; Thankarajan and Krishnankutty 1984). A weak band observed at $\sim 1620 \text{ cm}^{-1}$ in the spectra of the metal complexes is probably due to $\nu \text{C}=\text{N}$, which might have been masked by the stronger carbonyl bands in the spectra of the ligands. A very broad band of the ligand at $3500\text{--}2400 \text{ cm}^{-1}$, due presumably to hydrogen-bonded OH/NH stretching, is replaced in the spectra of the metal complexes by a weaker broad band at $3550\text{--}3350 \text{ cm}^{-1}$, attributable to the amide N-H, and coordinated water. In the case of iron(III) complexes, their coordinated OH groups caused strong absorption and peak formation at $\sim 3570 \text{ cm}^{-1}$, in addition to a band at $\sim 1130 \text{ cm}^{-1}$ for Fe-OH bonding (Nakamoto 1978).



$H_2PAA:: R_1 = R_2 = CH_3$
 $H_2PBA : R_1 = CH_3; R_2 = C_6H_5$
 $H_2PDM : R_1 = R_2 = C_6H_5$

$M = Cu^{2+}, Ni^{2+}, Pd^{2+}, Fe^{3+}$

Chart 1.

3.2 1H NMR spectra of palladium(II) complexes

Further evidence for the bonding mode of the ligands (structure II) is provided by the 1H NMR spectra of their palladium(II) complexes. The non-equivalence of the two methyl protons (2.30 and 2.65 δ) of H_2PAA (Thankarajan *et al* 1986) persists in its complex, (2.35 and 2.72 δ). A low field broad one-proton signal at $\sim 14\delta$ in the spectra of all the three ligands for hydrogen-bonded NH disappeared in the spectra of the complexes, indicating replacement of the NH proton during metal chelation. A comparatively broad one-proton signal at $\sim 5.4\delta$ for the amide proton of the phthalhydrazide ring is present in the spectra of the ligands and of the metal complexes. The signal for the OH proton of the ligands could not be located in their spectra, presumably due to fast exchange.

3.3 Stability of copper(II) complexes

Order of stability on the basis of polarographic reduction potentials (table 2) of the three copper(II) complexes is $-[Cu(PAA)(H_2O)] > [Cu(PBA)(H_2O)] > [Cu(PDM)(H_2O)]$. Cross conjugation by pendant group(s) seems responsible for the destabilisation of metal chelates of H_2PBA and H_2PDA . Data for $\nu(Cu-N)$ and $\nu(Cu-O)$ from far IR spectra of the complexes (table 2) are in agreement with the stability order.

Table 2. Half-wave potentials and far IR data of copper(II) complexes.

Complex	$E_{1/2}$ (V) First wave	$\nu_{\text{Cu-N}}$ (cm^{-1})	$\nu_{\text{Cu-O}}$ (cm^{-1})
[Cu(PAA) (H ₂ O)]	-0.380	560	460
[Cu(PBA) (H ₂ O)]	-0.365	548	453
[Cu(PDM) (H ₂ O)]	-0.350	535	450

Table 3. Mössbauer spectral data of iron(III) complexes.

Complex	δ (mm/s)	ΔE_Q (mm/s)
[Fe(PAA) (OH) (H ₂ O) ₂]	+0.331	0.963
[Fe(PBA) (OH) (H ₂ O) ₂]	+0.368	0.959
[Fe(PDM) (OH) (H ₂ O) ₂]	+0.389	0.955

3.4 Mössbauer spectra of iron(III) complexes

Effect of cross resonance by pendant group on d electron delocalisation with the metal chelate ring was examined from Mössbauer spectral data of the iron(III) complexes. It is evident from observed δ values (table 3) that d electron delocalisation with the chelate ring decreases when the pendant groups of chelate ring are changed from acetyl to benzoyl, and methyl to phenyl. Thus, it is evident that any cross conjugation of the metal chelate ring is not conducive to d electron delocalisation with the ring. Observed ΔE_Q values reveal that increased d electron delocalisation with the chelate ring increases the field gradient at the nucleus.

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Kinetic model for micellar catalysed hydrolysis of esters – biomolecular reactions

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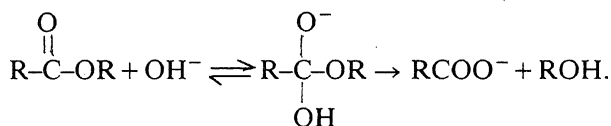
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Abstract. The cationic micelles of cetyltrimethylammonium bromide, cetyldibenzylammonium chloride and cetylpyridinium chloride stabilize the tetrahedral intermediate formed in the hydrolysis of carboxylic esters (e.g. *p*-nitrophenylbenzoate) to a greater extent, preferring a B_{AC2} mechanism, than the anionic intermediate formed in the hydrolysis of *m*-nitrophenyl-N-N-diphenylphosphorodiamidate, which prefers a E_{1cB} mechanism. The co-operative index, n_1 , calculated for these reactions is greater than 1 indicating that the substrate induced micellation is responsible for the observed catalysis. Based on the present kinetic model for a bimolecular reaction, the fraction of substrate and nucleophile bound to the micelle have been calculated. The above results suggest that reaction occurs between the substrate solubilised into the micelle and the nucleophile residing at the Stern layer rather than at the micelle-water interface. The equilibrium constant, and critical micelle concentration, evaluated using the present model are in agreement with the values obtained by using earlier models, suggesting a method of evaluating these parameters from kinetic data only.

Keywords. Cationic micelles; catalysis in ester hydrolysis; kinetic model for bimolecular reaction; equilibrium constant; critical micelle concentration.

1. Introduction

The hydrolysis of esters generally involves an attack of the anion OH^- on the carboxyl carbon of the ester resulting in a negatively charged tetrahedral intermediate



Therefore, the acceleration or deceleration of the deacylation reactions in the presence of micelles can be rationalised by considering the forces that would stabilize or destabilize the tetrahedral intermediate.

In the present work, the micellar influences on the kinetics of the hydrolysis of carboxyl esters, viz., *p*-nitrophenylbenzoate (PNPB), *p*-nitrophenyl-*p*-nitrophenylacetate (PA), *p*-nitrophenyl-*p*-chlorobenzoate (PCB) and *p*-nitrophenyl-N-phenylcarbamate (PCM), sulphate esters – *p*-nitrophenyltoluene-sulphonate (PTS) and *p*-nitrophenylphenylmethanesulphonate (PMS), and a phosphate ester – *m*-nitro-

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phenyl-N-N-diphenylphosphorodiamidate (PDI), have been studied in detail. The cationic micelles, formed from cetyltrimethylammonium bromide (CTAB), cetyl-dimethylbenzylammonium chloride (CDBAC), and cetylpyridinium chloride (CPC), stabilize the tetrahedral intermediate and hence catalyse the hydrolysis of esters. In what follows, a concise account of the catalysis by each one of the cationic micelles in the hydrolysis of the above esters has been discussed.

2. Results and discussion

The influence of cationic-micelle-forming detergents, CTAB, CDBAC and CPC, has been investigated in the hydrolysis of esters in borax-buffer media at $30^\circ \pm 0.1^\circ\text{C}$ and an ionic strength 0.10 mol dm^{-3} .

2.1 Effect of added CTAB, CDBAC and CPC on the hydrolysis of esters

The cationic micelles of CTAB exhibit maximum rate enhancement in the case of PMS and exert minimum effect in the case of PDI. The rate constant (k_{obs}) versus [CTAB] profile for each ester exhibits a maximum which is characteristic of bimolecular reactions and the maximum rate benefit is observed at a particular concentration of CTAB for each one of the esters used (table 1). But with CDBAC, maximum rate acceleration is observed in the hydrolysis of PCB (100-fold) (table 2), while the rate enhancement observed in the hydrolysis of PTS is minimum (15-fold). The reaction of PA attains its maximum rate even at a concentration of CDBAC lower than its (critical micelle concentration) c.m.c. ($1.20 \times 10^{-4} \text{ M}$ under the present reaction conditions). Phenyl acetates have been shown to hydrolyse via E_{1cB} path in the presence of cationic micelles (Tagaki *et al* 1976; Yano *et al* 1979) and therefore, the observed higher rate maximum for PA even at low concentrations of CDBAC is not unexpected (Al-Lohedan and Bunton 1981).

Table 1. Effect of CTAB on the rate of hydrolysis of esters.

$10^4[\text{CTAB}]\text{M}$	PNPB ^a	PTS ^b	PMS ^c	PCB ^a	PDI ^{d,e}
0.00	5.5	5.0	3.4	5.2	1.06
0.50	6.8	8.4	4.6	7.1	—
1.00	7.4	8.4	3.3	15.1	—
2.5	9.1	10.6	10.5	—	—
5.0	12.1	35	25	41	—
10.0	12.3	25	41	37	2.3
20	—	25	48	—	2.3
50	—	—	45	—	2.7
100	—	—	—	—	2.8

[ester] = $1.50 \times 10^{-5} \text{ M}$; pH = 9.2; [NaCl] = 0.10 M ; temperature = 30°C .

^a $10^4 k_{\text{obs}} \text{ s}^{-1}$; ^b $10^7 k_{\text{obs}} \text{ s}^{-1}$; ^c $10^3 k_{\text{obs}} \text{ s}^{-1}$; ^d $10^5 k_{\text{obs}} \text{ s}^{-1}$; ^e [PDI] = $3.0 \times 10^{-4} \text{ M}$ in 20% aqueous CH_3CN .

Table 2. CDBAC influenced hydrolysis of esters.

$10^4[\text{CDBAC}]/\text{M}$	PNPB ^a	PTS ^b	PMS ^c	PA ^d	PCB ^e
0.00	1.42	2.4	1.34	0.57	0.193
0.50	2.2	2.2	2.1	0.86	—
1.00	3.2	4.1	4.7	2.8	0.188
2.0	23	9.5	7.1	9.6	0.47
5.0	28	25	85	17.9	0.95
10.0	37	36	105	17.9	1.64
20	24	14.5	68	13.3	14.0
50	17.2	13.8	42	12.9	20
100	—	10.5	—	—	14.4

[ester] = 1.50×10^{-5} M; pH = 9.2; temperature = 30°C.^a $10^4 k_{\text{obs}} \text{ s}^{-1}$; ^b $10^7 k_{\text{obs}} \text{ s}^{-1}$; ^c $10^3 k_{\text{obs}} \text{ s}^{-1}$; ^d $10^2 k_{\text{obs}} \text{ s}^{-1}$; ^e $10^3 k_{\text{obs}} \text{ s}^{-1}$.**Table 3.** Effect of CPC on the hydrolysis of esters.

$10^4[\text{CPC}]/\text{M}$	PNPB ^a	PTS ^b	PMS ^c	PA ^d	PCB ^d	PDI ^{e,f}
0.00	1.42	2.4	1.34	5.7	0.193	1.64
0.050	2.8	—	—	36	—	1.77
0.100	3.1	—	2.1	60	—	—
0.50	3.6	2.1	2.2	116	1.02	2.5
1.00	5.6	4.0	7.9	134	2.2	2.9
2.0	9.5	6.2	21	108	4.7	—
5.0	12.2	8.0	58	—	11.7	2.1
10.0	19.4	11.1	109	—	14.6	—
20	30	50	132	—	29	—
50	22	50	108	—	15.0	—

[ester] = 1.50×10^{-5} M; pH = 9.2; temperature = 30°C.^a $10^4 k_{\text{obs}} \text{ s}^{-1}$; ^b $10^7 k_{\text{obs}} \text{ s}^{-1}$; ^c $10^3 k_{\text{obs}} \text{ s}^{-1}$; ^d $10^3 k_{\text{obs}} \text{ s}^{-1}$; ^e $10^4 k_{\text{obs}} \text{ s}^{-1}$ for the hydrolysis of [PDI] = 3.0×10^{-4} M by 1.0×10^{-2} M OH^- in 20% aqueous CH_3CN .

Cetylpyridinium chloride (CPC) catalyse the hydrolysis of these esters (table 3) even at submicellar concentrations and it is more effective in catalysing the hydrolysis of PCB (150-fold increase in rate) while it is less efficient with PDI (only 2-fold increase in rate).

2.2 Co-operativity index in micellar catalysed reactions

Binding of additional substrate to oligomeric enzymes may increase or decrease the observed reaction rate and by analogy the co-operativity between the surfactant molecules and the substrate may account for micellar catalysis. For such a reaction, a co-operativity model has been proposed by Piskiewicz (1977) and the equation arrived at from such a model is

$$\log [(k_{\text{obs}} - k_0)/(k_m - k_{\text{obs}})] = n \log [D] - \log K_D. \quad (1)$$

From the data in tables 1, 2 and 3, $\log [(k_{\text{obs}} - k_0)/(k_m - k_{\text{obs}})]$ versus $\log [\text{detergent}]$ graphs have been drawn. Fairly linear correlations are observed and the values of co-operativity index, n , and $\log [D]_{50}$ derived therefrom are summarised in table 4.

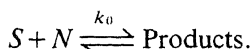
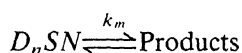
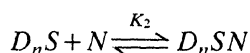
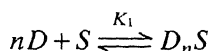
Table 4. Piskiewicz's co-operativity values.

Substrate	Detergent	n	$\log [D]_{50}$	$[D]_{50}$	K_D
PNPB	CTAB	1.6	-3.8	1.70×10^{-4}	1.04×10^{-6}
PTS	CTAB	0.63	-2.6	2.7×10^{-3}	2.5×10^{-2}
PMS	CTAB	2.3	-3.3	5.2×10^{-4}	3.1×10^{-8}
PCB	CTAB	2.1	-3.7	2.1×10^{-4}	1.39×10^{-8}
PDI	CTAB	0.39	-3.4	3.6×10^{-4}	4.6×10^{-2}
PNPB	CDBAC	1.28	-3.7	1.92×10^{-4}	1.75×10^{-5}
PTS	CDBAC	2.3	-3.5	3.6×10^{-4}	1.78×10^{-8}
PMS	CDBAC	0.87	-4.0	9.2×10^{-5}	3.1×10^{-4}
PA	CDBAC	2.8	-4.7	2.0×10^{-5}	6.3×10^{-14}
PCB	CDBAC	2.2	-3.7	2.0×10^{-4}	7.4×10^{-9}
PNPB	CPC	0.64	-3.0	9.5×10^{-4}	1.16×10^{-2}
PTS	CPC	1.19	-2.7	1.94×10^{-3}	5.9×10^{-4}
PMS	CPC	1.89	-3.3	5.0×10^{-4}	5.7×10^{-7}
PA	CPC	1.06	-4.8	1.52×10^{-5}	9.8×10^{-6}
PCB	CPC	1.28	-3.1	8.5×10^{-4}	1.18×10^{-4}
PDI	CPC	1.04	-4.2	6.1×10^{-5}	4.2×10^{-5}

The values of n are in keeping with the earlier observations (Piskiewicz 1977) and a value $n > 1$ predicts substrate induced micellisation which would have been responsible for the observed catalysis in the presence of detergents at submicellar concentrations. $[D]_{50}$ is also in good agreement with the experimental observations. From the intercept, the decomposition constant, K_D , has been evaluated. Although this treatment predicts that the number of surfactant monomers in each aggregate is of the order of 1-5, making the size of the micelle considerably smaller than typical micelles, the approach may be useful in indicating the way in which substrates may assist micellisation or comicellisation.

2.3 Model for bimolecular micellar catalysed reactions

The acceleration of reaction rates in the presence of micelles have been attributed on most occasions to the increase in concentration of reactants on the micellar phase, and the association in micellar phase has been explained quantitatively in terms of the binding constants. Earlier models in vogue for the evaluation of binding constants in micellar catalysed reactions require a parameter such as volume of the Stern layer or the micellised nucleophile concentration etc., which is difficult to determine kinetically. Therefore, this paper attempts to evaluate the binding constants of reactants with the micelle from the kinetically accessible parameters above. According to the following simplified scheme (I),



where D , S and N refer to the detergent monomer, substrate and the nucleophile while D_nS and D_nSN refer to the binary and ternary complexes. The products are assumed to result from the reaction between the substrate and the nucleophile, in aqueous medium as well as in the micellar phase, by the decomposition of ternary complex. The rate-law for this scheme is,

$$\text{rate} = k_0[S]_f[N]_f + k_m[D_nSN], \quad (1)$$

where f refers to free species. As

$$[D_nSN] = K_2[D_nS][N]_f,$$

$$[D_nS] = K_1[D]^n[S]_f, \text{ and}$$

free substrate concentration $[S]_f = [S]_{\text{total}} - [D_nS]$, the concentration of D_nS and D_nSN can be given as,

$$[D_nS] = K_1[D]^n[S]_T / (1 + K_1[D]^n),$$

$$[D_nSN] = K_1 K_2 [D]^n [S]_T [N]_f / (1 + K_1[D]^n).$$

Assuming $[N]_f = [N]_{\text{total}} - [D_nSN]$, the concentration of ternary complex, D_nSN , $[N]_f$ and $[S]_f$ are evaluated. On introducing these in 1, it becomes

$$\text{rate} = \frac{k_0[S]_T[N]_T + k_m K_1 K_2 [D]^n [S]_T [N]_T}{1 + K_1[D]^n \{1 + K_2[S]_T\}},$$

or

$$k_{\text{obs}} = \frac{k_0 + k_m K_1 K_2 [D]^n}{1 + K_1[D]^n \{1 + K_2[S]_T\}} \quad (2)$$

This form of equation is identical to those derived by Martinek *et al* (1977) and Bunton *et al* (1978). This model also predicts constancy in k_{obs} values at high detergent concentrations.

Equation 2 takes the form

$$\frac{k_{\text{obs}} - k_0}{k_{\text{obs}}} \frac{1}{[D]^n} = K_1 K_2 \frac{k_m}{k_{\text{obs}}} K_1 \{1 + K_2[S]_T\}, \quad (2)$$

which predicts a linear relationship between $(k_{\text{obs}} - k_0)/k_{\text{obs}} \cdot (1/[D]^n)$ with k_m/k_{obs} and it is realised in various systems. Using the value of n obtained from Piskiewicz's co-operativity model, with the help of the present model, K_1 is calculated without recourse to the c.m.c. value which is a variable parameter. However, this model does not consider the effect of counter ions nor the interaction of products with the micelles. When the proposed model is applied to several systems, the value of K_1 and the intercept in all the cases are almost the same in magnitude as $K_2[S]_T \ll 1$ (table 5). The evaluated K_1 values are also in good agreement with those obtained from the Piskiewicz model and an abnormal value of K_1 from both the models would be due to the assumption that the substrate induces micellisation in which case there should be very strong association of the substrates with the micelles.

Table 5. Evaluation of binding constants using present model.

Reaction	n^*	intercept**	K_1^*	K_2^{**}	
Electron transfer from <i>n</i> -butyl ferrocene to Fe^{3+} in presence of NaIS	1.07	-9.4×10^2	9.4×10^2 (5.7×10^2)	0.69	(Bunton and Cerichelli 1980)
Hydrolysis of <i>p</i> -nitro-phenyl acetate in presence of CTAB	1.72	-1.48×10^4	1.48×10^4 (3.8×10^4)	1.35	(Beheme <i>et al</i> 1965)
Hydrolysis of <i>p</i> -nitro-phenylhexanoate in presence of CTAB	2.8	-2.3×10^8	2.3×10^8 (1.3×10^8)	0.90	(Beheme <i>et al</i> 1965)
Hydrolysis of methyl-ortho benzoate in presence of NaIS	3.0	-1.15×10^8	1.15×10^8 (4.4×10^7)	0.43	(Beheme <i>et al</i> 1965)
Hydrolysis of <i>p</i> -nitro-phenylhexanoate in presence of TDTACI	4.9	-5.5×10^{12}	5.5×10^{12} (6.3×10^{12})	1.09	(Romsted and Cordes 1968)
Hydrolysis of <i>p</i> -nitro-phenyl acetate in presence of TDTACI	2.5	-9.3×10^5	9.3×10^5 (1.14×10^6)	1.05	(Romsted and Cordes 1968)
Acid hydrolysis of <i>N</i> -(tri-fluoroacetyl)indole in presence of NaIS	4.1	-4.3×10^9	4.3×10^9 (6.1×10^9)	1.06	(Cipicianni <i>et al</i> 1981)

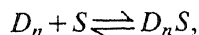
* From Piskiewicz's co-operativity equation; ** using (2) derived from present model; values in parentheses are obtained from the intercept of Piskiewicz's equation.

The low values of K_2 ($K_2 \ll K_1$) suggest that $[N]_f = [N]_{\text{total}}$, and therefore, the nucleophile is present almost in full in the bulk phase – an idea which parallels the assumptions of Romsted (1977) and the opinion of Reeves (1975).

In the light of the above conclusion we have to conjecture that the reaction takes place between the substrate solubilised into a micelle and the nucleophile residing at the Stern layer of the micelle without being bound strongly to it at the micelle-water interface. This also gains support from Menger's (1971) work.

Therefore, the observed catalysis of reactions by cationic micelles might have been the result of a proper orientation of the substrate the carbonyl group being polar residing at the Stern layer with the non-polar portions adsorbed into the cone for facile reaction with the nucleophile. However, this conclusion cannot be proved beyond doubt with the data available.

The micelle-substrate binding constant has been separated from other equilibrium constants by modifying the scheme as



This leads to the modified expression

$$\frac{k_{\text{obs}} - k_0}{k_{\text{obs}}} \frac{1}{[D_n]} = K_1 K_2 \frac{k_m}{k_{\text{obs}}} - K_1 \{1 + K_2 [S]_T\}. \quad (3)$$

Table 6. Comparison of binding constants (K/N) from Menger's equation and the present model.

Reactions	a*	b
<i>Hydrolysis of</i>		
PNPB in presence of CTAB	7.4×10^3	1.04×10^4
PMS in presence of CTAB	1.36×10^2	62
PNPB in presence of CDBAC	2.1×10^4	2.2×10^4
PCB in presence of CDBAC	7.8×10^4	7.7×10^4
PTS in presence of CDBAC	2.3×10^3	3.0×10^3
PA in presence of CDBAC	4.1×10^3	3.6×10^3
PMS in presence of CDBAC	1.0×10^3	2.2×10^3
PNPB in presence of CPC	6.8×10^3	9.4×10^3
PCB in presence of CPC	2.3×10^2	1.56×10^3
PMS in presence of CPC	4.5×10^3	5.1×10^3

* in calculating the binding constants, c.m.c. values from present model have been used;

a) binding constant (K/N) using equation 3

b) binding constant (K/N) calculated using the equation of Menger and Portnoy (1967)

This equation has also been applied to different systems and the derived data have been collected in table 6. The consequence of the much lower values of K_2 , i.e. the binding of the nucleophile with micelles is negligible, conveys that only the substrate is distributed between micellar and aqueous phases. In such case, the earlier treatment of Menger and Portnoy (1967) for unimolecular reactions should also hold good for bimolecular reactions. Table 6 includes data obtained by using the equation by Menger and Portnoy (1967). A fairly good agreement between the values in columns *a* and *b* of table 6, upholds the applicability of (3) to bimolecular micellar catalysed reactions.

3. Experimental

A detailed procedure for the preparation of the esters used in the present work is included in our early paper (Raghavan and Srinivasan 1984). The detergents were purified till the c.m.c. agreed with the reported value (Fendler and Fendler 1975).

All the reactions were carried out at pH = 9.2 in 0.050 M borax buffer in 0.10 M NaCl at 30°C unless otherwise mentioned. Small amount of H_3CCN was used in making up the substrate solution and pure water was generally used as the solvent. The pH of the buffer solution was adjusted in the presence of detergent with a digital pH meter. The critical micelle concentrations were measured for these detergents spectrophotometrically, using the dye eosine ($\lambda_{max} = 540 \text{ nm}$), as probe. (c.m.c. value for CTAB, CDBAC and CPC in borate buffer at pH = 9.2 is around $1.0 \times 10^{-4} \text{ M}$.) Reactions were monitored by following the release of *p*- (or) *m*-nitrophenoxide ion at 400 nm using a Carl-Zeiss VSU 2P spectrophotometer. From the infinite values determined after nine half-lives, specific rates were evaluated from the slopes of the regression lines for correlations of $\log [A_\infty - A_t]$ vs. time. The linear regression analysis was performed on a micro-programmable calculator (Hindustan Computers).

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Substituent effects on carbon-13 NMR chemical shifts of side chain carbonyl carbons of 4-substituted 1-naphthamides

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Abstract. Substituent induced ^{13}C NMR chemical shifts of side chain carbonyl carbons of several 4-substituted 1-naphthamides have been measured in $\text{DMSO}-d_6$ solvent. Analysis of the substituent induced chemical shifts by the DSP equation gave the regression equation. Both ρ_I and ρ_R values were negative. The negative sign on ρ_I term indicates the operation of a reverse substituent effect and that π -polarisation is the important mechanism for the transmission of substituent effects by inductive effect. The *peri*-hydrogen interaction in naphthamides forces the amide group out of the plane of the naphthalene ring.

Keywords. Naphthamides; substituent chemical shifts; reverse substituent effect; π -polarisation.

1. Introduction

In recent years much attention has been paid to correlate the substituent induced ^{13}C NMR chemical shifts of aromatic compounds with the Hammett substituent constants. The effect of substituents in the ring on the chemical shifts of side chain carbon is of obvious interest, especially in those cases where the side chain carbon is capable of conjugating with the ring. Correlation of ^{13}C NMR chemical shifts of π -bonded groups conjugated with substituted aryl rings have appeared for several classes of compounds such as styrenes (Dhami and Stothers 1965; Hamer *et al* 1973), phenylacetylenes (Dawson and Reynolds 1975), 1-aryl-propenes and propynes (Izawa *et al* 1973), benzylidene anilines (Inamoto *et al* 1974), benzonitriles (Bromilo and Brownlee 1975), and α,β -unsaturated sulphones (Srinivasan *et al* 1986). The ^{13}C NMR chemical shifts of carbonyl groups conjugated with aryl rings have generally been observed to be 'insensitive' to substituent effects (Mathias 1966; Dhami and Stothers 1965, 1967) and only limited reports of their linear free energy relationships have appeared. Benzoic acids exhibit carbonyl carbon ^{13}C chemical shifts of range 2.4 ppm (Niwa and Yamazaki 1974). A series of N-phenacylpyridinium bromides (Harch *et al* 1977) with substituents in the pyridine ring exhibit greater sensitivity for the carbonyl resonance.

The substituent induced chemical shifts (SCS) of sp^2 and sp carbons directly bonded to the ring have been observed to show 'reverse substituent effects' (Bromilow *et al* 1977, 1981; Brownlee and Craik 1981; Srinivasan *et al* 1986), i.e., electron-attracting substituents apparently increase the electron density on the

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carbon concerned whereas electron-releasing substituents decrease it. This phenomenon has been attributed to the polarisation of the π -system of the side chain. Almost all studies in this area have involved carbon bonded to oxygen, nitrogen or other carbon atoms (Butt and Topsom 1980, 1982; Solcaniova *et al* 1976, 1980). In this study, ^{13}C NMR chemical shifts of carbonyl carbons of several 4-substituted 1-naphthamides have been measured and the SCS have been analysed by the DSP equation. The results of the analysis have been compared with those of the benzamides.

2. Experimental

Substituted 1-naphthoic acids were prepared by the hypobromite oxidation of the corresponding acetophenones (Ananthakrishna Nadar and Gnanasekaran 1978). The acids were converted into amides by the acid chloride method. Carbon-13 NMR spectra were run on Nicolet NT-300 spectrophotometer at 75.45 MHz using 5 mm sample tubes. The solvent is DMSO- d_6 and 16 K data points were used for all the samples. The chemical shifts were measured relative to internal TMS standard and are accurate within 0.02 ppm.

3. Results and discussion

The carbonyl carbon of aromatic amide group resonates near 170 ppm. These are well removed from other carbons in the spectrum and these absorptions are all of low intensity due to minimal nuclear overhauser enhancement and to their relatively long relaxation times. So these carbons can be unequivocally assigned. The side chain carbonyl carbon chemical shifts of several 4-substituted 1-naphthamides are presented in table 1 along with the relevant data for para-substituted benzamides.

Examination of data in table 1 shows that substituents have a relatively small influence on ^{13}C chemical shifts ($\Delta\delta = 1.6$ ppm). All substituents cause upfield shift of the carbonyl carbon resonance compared to unsubstituted compound. The observed upfield shift for electron-attracting substituents is contrary to the

Table 1. Carbon-13 NMR chemical shifts of carbonyl carbons of naphthamides and benzamides.

Substituent	4-Substituted 1-naphthamides							
	OCH_3	CH_3	H	F	Cl	Br	I	NO_2
δ (ppm)	170.60	170.82	170.89	169.80	169.88	169.94	170.01	169.28
$\Delta\delta$ (ppm)	-0.29	-0.07	0.00	-1.09	-1.01	-0.95	-0.88	-1.61
para-substituted benzamides								
Substituent	OCH_3	CH_3	H	F	Cl	Br	NO_2	
δ (ppm)	167.85	168.20	168.29	167.27	167.22	167.32	166.64	
$\Delta\delta$ (ppm)	-0.44	-0.09	0.00	-1.02	-1.07	-0.97	-1.65	

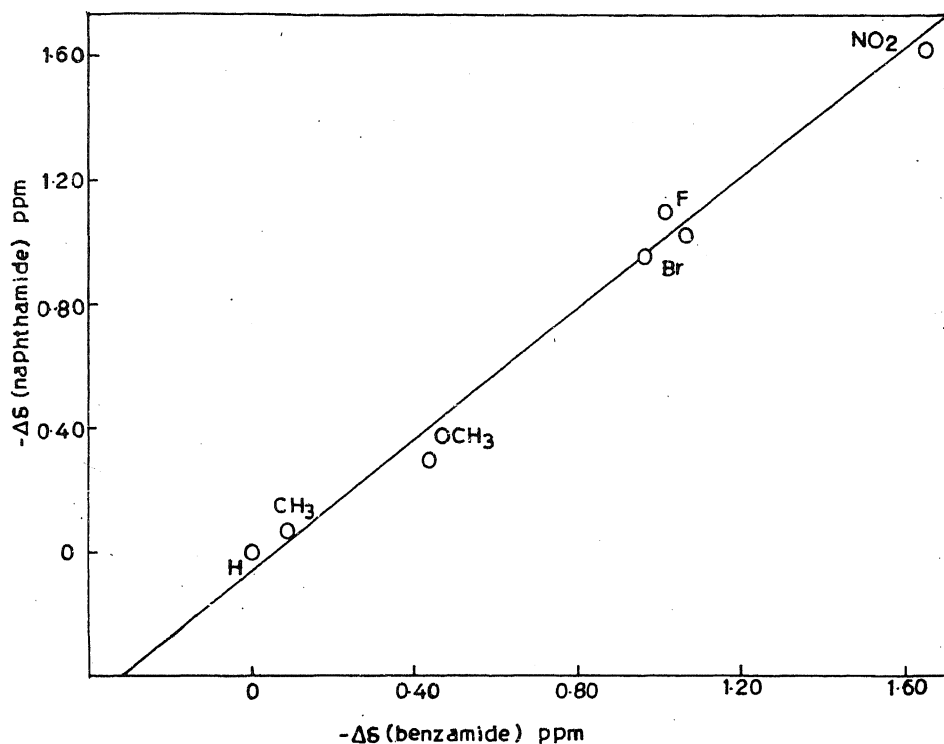


Figure 1. Plot of SCS of 4-substituted 1-naphthamides versus para-substituted benzamides. $\Delta\delta$ (ppm) values for benzamides are from Bromilow *et al* (1981).

expectation that they should withdraw electron density, decrease the shielding and cause a down-field shift. The plot of SCS of 4-substituted 1-naphthamides versus SCS of para-substituted benzamides is linear (figure 1) with a slope of 1.00 ($r = 0.994$; s.d. = 0.07). This indicates that the mechanism for transmission of electronic effects of the substituents in these two series is similar.

The SCS were analysed by the single parameter equation and the correlations obtained were poor. Since single parameter equation has failed, the SCS have been analysed by the DSP equation in the form

$$\text{SCS} = \rho_I \sigma_I + \rho_R \sigma_R \quad (1)$$

The DSP methods (Ehrens on 1964) provides the relative magnitudes of various modes of transmission of substituent effects like ρ_I and ρ_R values, which are not obtainable from single parameter treatment. The DSP analysis gave the following regression equation

$$\begin{aligned} \text{SCS} = & -2.25\sigma_I - 0.51\sigma_R^{(BA)} \\ & \pm 0.15 \quad \pm 0.15 \quad (n = 8; R = 0.990) \end{aligned} \quad (2)$$

As seen from the results of the regression analysis, the inductive effect contributes more to the chemical shifts of the carbonyl carbons than the resonance effect. The ρ_I term is negative and its magnitude is quite comparable to that of para-substituted

benzamides ($\rho_I = -2.4$). The negative sign on ρ_I term indicates the operation of reverse SCS effect. This is due to the fact that π -polarisation of the carbon-oxygen bond is the major contribution to the inductive component of ^{13}C SCS values (Bromilow *et al* 1981). This type of polarisation is the 'localised polarisation' involving the separate polarisation of the side-chain as shown in chart 1.

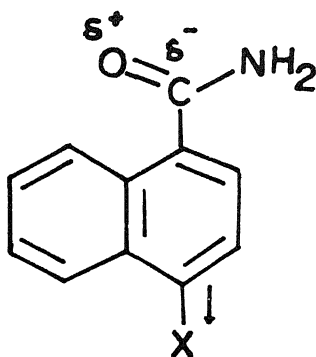


Chart 1.

In chart 1, if X is an inductive electron-attracting substituent, a dipole on X or near C-X is set up, the interaction of this dipole through space of the molecular cavity results in the polarisation shown. The net result is that the inductive electron-attracting substituent increases the electron density at the carbonyl carbon and hence increases the shielding to cause upfield shift.

Bromilow *et al* (1981) have shown that for series of the general form $\text{X}-\text{C}_6\text{H}_4-\text{COZ}$, the inductive effect of X on SCS of the side chain carbonyl carbon is largely determined by localised π -polarisation of $\text{C}=\text{O}$ π -electrons and is independent of the adjacent Z group. On the other hand, the resonance effect of X on SCS varies from one series to another, and is determined by both the inductive and resonance effects of the Z group. When Z is a strong resonance donor ($\text{Z}=\text{NH}_2$), ρ_R is negative, and when Z is neutral ($\text{Z}=\text{H}$) or inductive donor ($\text{Z}=\text{CH}_3$), ρ_R is positive. The observed negative ρ_R value for the present system is in accordance with the observations reported by Bromilow *et al* (1981).

The carbonyl carbon resonance of 2-naphthamide (168.15 ppm) is very close to that of benzamide (168.29 ppm). Compared to benzamide and 2-naphthamide the carbonyl carbon resonance of 1-naphthamide (170.89 ppm) occurs at down field. This may be due to the *peri*-hydrogen interaction in 1-naphthamide. The *peri*-hydrogen forces the amide group out of the naphthalene ring and thereby reduces the conjugation with the aromatic ring. This decrease in conjugation increases the deshielding of the carbonyl carbon and hence downfield resonance occurs.

It is reasonable to assume that the conjugative interaction between the carbonyl group and the aromatic ring will be maximum, if the dihedral angle, θ , between the aromatic ring and the carbonyl group is zero. This interaction is minimum if $\theta = 90^\circ$ (chart 2).

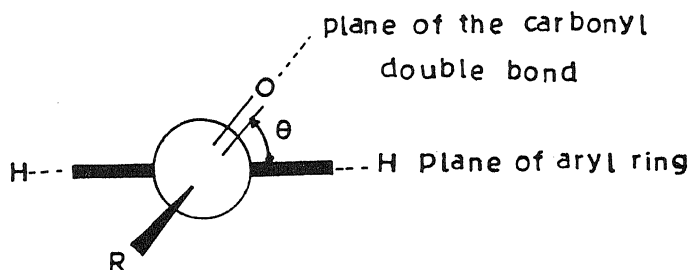


Chart 2.

Table 2. Dihedral angle in 4-substituted 1-naphthamides.

Substituent	OCH_3	CH_3	H	F	Cl	Br	NO_2
θ°	21.8	21.2	21.1	20.8	21.4	21.2	21.3

The chemical shifts of carbonyl carbon in benzene derivatives can be taken as that typical for a planar system where θ is zero. A relationship between the interplanar angle θ and the carbonyl carbon chemical shift has been proposed based on model compounds with complete ($\theta = 0^\circ$) and minimum ($\theta = 90^\circ$) orbital overlap (Dhami and Stothers 1964). The observed carbonyl carbon resonance δ_o^x , the interplanar angle θ and the chemical shift δ_b^x for benzene analogues are related by the following expression:

$$\cos^2 \theta = [(\delta_b^x + 20) - \delta_o^x] / 20. \quad (3)$$

Substituting the δ_b^x (Bromilow *et al* 1981) and δ_o^x values (present data) in (3), θ values are evaluated for 1-naphthamide and several 4-substituted 1-naphthamides (table 2). In all the naphthamides, the amide group is out of the plane of the naphthalene ring to an extent of 21° .

Acknowledgements

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Kinetics of oxidation of ethylenediamine tetraacetic acid by aromatic N-bromamines in buffer medium

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Abstract. Kinetics of oxidation of disodium ethylene-diamine-tetraacetic acid (EDTA) by bromamine-B (BAB) and bromamine-T (BAT) was investigated at 30°C in acetate buffer of pH 5. The oxidation behaviour is similar, with a first-order dependence of rate on [oxidant] and fractional orders in [EDTA] and $[H^+]$. The influence of the reaction products, halide ions, ionic strength and dielectric constant of medium on the rate has been studied. A possible mechanism is suggested.

Keywords. Bromamine-T; bromamine-B; kinetics; EDTA; acetate buffer.

1. Introduction

The disodium salt of ethylenediaminetetraacetic acid (Na_2H_2Y or EDTA) is well-known as a chelating agent in complexometry and is employed for identification and differential estimation of a number of metal ions. Although this aspect of EDTA chemistry is described in great detail in literature, very little is known about the behaviour of oxidants towards this compound. Hanna *et al* (1969) have shown that HCHO and CO_2 are formed in the oxidation of EDTA by Ce(IV). Similar results were obtained by Rao (1970). Sanehi *et al* (1973) have carried out a systematic investigation of the oxidation of EDTA with chloramine-T (CAT) in acetate buffer medium, but the products have not been identified. The iron(III) catalysed oxidation of EDTA in aqueous solution at elevated temperatures (100–170°C) has shown the formation of ethylene triacetic acid (Motekaitis *et al* 1980). Formation of HCHO, CO_2 and N-hydroxy methylethylene diamine was observed during the oxidation of EDTA with a suspension of PbO_2 in H_2SO_4 (Ito *et al* 1980).

The chemistry of N-halo-N-sodiosulphonamides in aqueous solution has received considerable attention and the existing literature on the prominent member of this class, namely chloramine-T has been reviewed (Campbell and Johnson 1978). Reports on the bromine analogues, bromamine-B or BAB and bromamine-T or BAT ($RNBr Na$ where $R = C_6H_5SO_2$ for BAB, and $p-CH_3C_6H_4SO_2$ for BAT), however, are scanty. As part of our broad programme (Mahadevappa *et al* 1984, 1985) on the mechanistic studies of aromatic bromamines, we now report the mechanistic aspects of oxidation of EDTA by BAB and BAT in acetate buffer of pH 5 at 30°C.

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2. Experimental

Preparation of BAB and BAT, and its purification have been reported in previous communications (Ahmed and Mahadevappa 1980; Nair and Indrasenan 1976). Aqueous solutions of the oxidants were standardized iodometrically and preserved in brown bottles. All other chemicals were of analytical grade. Triply distilled water was used throughout.

The reaction was carried out in glass-stoppered pyrex boiling tubes whose outer surface was coated black to eliminate photo-chemical effects. Requisite amounts of EDTA, sodium perchlorate and buffer (to keep the total volume constant for all runs) were taken in the tube and thermostated at 30°C for thermal equilibrium. A measured amount of oxidant solution was also thermostated at the same temperature and rapidly added to the mixture in the boiling tube. The progress of the reaction was monitored by iodometric determination of unreacted oxidant in a measured aliquot of the reaction mixture at different intervals of time. The course of the reaction was studied for two half-lives. The pseudo first-order rate constants (k') calculated were reproducible to $\pm 3\%$. Regression analysis of experimental data was carried out on a EC-75 statistical calculator.

Stoichiometry

Reaction mixtures under conditions, $[\text{EDTA}] \gg [\text{oxidant}]$, were equilibrated at 30°C in the presence of acetate buffer of pH 5 for 48 hours. Spot tests (Feigl 1956) indicated the presence of ethylene diamine (en) in the reaction mixture. The amine was transferred to the organic layer by solvent extraction with ether, which was then evaporated, and a concentrated aqueous solution of en was prepared. It was then estimated gravimetrically (Vogel 1961) as the complex $[\text{Cu en}_2][\text{HgI}_4]$. Quantitative estimation of amine was also carried out in a similar manner under conditions, $[\text{oxidant}] \gg [\text{EDTA}]$, after removing the excess oxidant with KI and thiosulphate. The results are shown below:

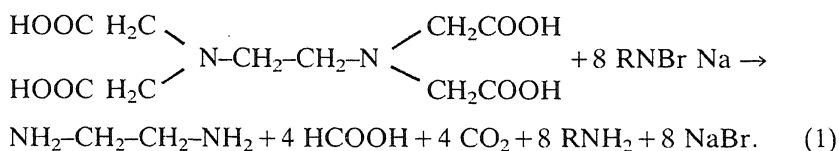
<i>EDTA taken</i> (m moles)	<i>BAT taken</i> (m moles)	<i>en theoretical</i> (m moles)	<i>en found</i> (m moles)
2.0	0.30	0.038	0.031
2.0	0.80	0.100	0.980
0.5	20.00	0.500	0.440
1.0	20.00	1.000	0.960
2.0	20.00	2.000	1.930
1.0	20.00	1.000	0.980
(with BAB)			

The stoichiometry of the reaction (1) was established under conditions by equilibrating reaction mixtures containing excess oxidant and then estimating the unreacted oxidant. The results are as follows:

EDTA taken = 5×10^{-4} mole

Time (hours)	Oxidant consumed (meq)		Number of eq. per mole of EDTA
	BAB	BAT	
20	7.50	7.50	15.0
25	7.70	7.74	15.4
30	7.95	7.91	15.9
40	8.02	8.00	16.0
48	8.07	8.01	16.1

The stoichiometry of the oxidation of EDTA with the bromamines can be represented as follows:



Benzene sulphonamide was detected by TLC. Formic acid was detected by the chromatographic acid procedure (Feigl 1956) after reducing with Mg and HCl, while CO_2 was identified by the conventional limewater test.

3. Results

The kinetics of oxidation of EDTA by BAB and BAT was investigated at several initial concentrations of the reactants in buffer medium at pH 5. Results obtained with BAT are shown in parentheses along with those obtained for BAB.

At constant pH, $[\text{EDTA}]_0$, plots of $\log [\text{oxidant}]$ versus time are linear ($r > 0.9980$) indicating a first-order dependence of rate on $[\text{oxidant}]_0$. The pseudo first-order rate constants k' are given in table 1. The rate increases with $[\text{EDTA}]$ (table 2) and a plot of $\log k'$ versus $\log [\text{EDTA}]_0$ is linear ($r > 0.9980$) with a slope of 0.64 (0.63). The rate of reaction decreases with increase in pH from 5.0 to 6.2 (table 3). A plot of $\log k'$ against pH is linear ($r > 0.9601$) with a slope of 0.45 (0.37). The effect of adding reaction product, benzene sulphonamide or toluene sulphonamide (RNH_2) to the reaction mixture had negligible influence on the rate. The ionic strength of the medium was varied by adding sodium perchlorate, but this had no effect on the rate of reaction. The dielectric constant (D) of the medium was varied by adding different proportions of methanol to the reaction mixture. Plots of $\log k'$ versus $1/D$ were linear ($r > 0.9937$) with a positive slope indicating charge dispersal in the transition state. Blank experiments showed that methanol is not oxidized by BAB or BAT under the experimental conditions.

The reaction rates were studied at different temperature (303–313 K). Plots of $\log k'$ versus $1/T$ were linear ($r > 0.9921$) from which the energy of activation E_a and other kinetic and thermodynamic parameters were calculated (table 4).

Addition of reaction mixture to acrylamide did not initiate polymerization showing the absence of free radicals.

Table 1. Effect of varying concentrations of oxidant on the rate of reaction in pH 5 buffer medium.

$[\text{EDTA}]_0 = 0.02 \text{ mol dm}^{-3}$; $\mu = 0.5 \text{ mol dm}^{-3}$;
temperature = 30°C

$10^3[\text{oxidant}]_0$	$k' \times 10^4 \text{ s}^{-1}$	
mol dm^{-3}	BAB	BAT
1.0	9.68	8.89
2.0	9.72	8.70
3.0	9.70	8.84
4.0	9.73	8.62
5.0	9.74	8.67
6.0	9.70	8.52

Table 2. Effect of varying concentrations of EDTA on the rate of reaction in pH 5 buffer medium.

$[\text{BAB}][\text{BAT}] = 0.003 \text{ mol dm}^{-3}$; $\mu = 0.5 \text{ mol dm}^{-3}$;
temperature = 30°C

$10^2[\text{EDTA}]$	$k' \times 10^4 \text{ s}^{-1}$	
mol dm^{-3}	BAB	BAT
1.0	6.14	5.56
1.5	8.13	7.62
2.0	9.70	8.84
2.5	11.3	10.0
3.0	13.2	11.6
4.0	15.0	13.7
5.0	17.0	15.4

Table 3. Effect of varying pH on the rate of oxidation of EDTA by BAB (BAT) in pH 5 medium.

$[\text{BAB}][\text{BAT}] = 0.003 \text{ mol dm}^{-3}$; $[\text{EDTA}] = 0.02 \text{ mol dm}^{-3}$;
temperature = 30°C $\mu = 0.5 \text{ mol dm}^{-3}$

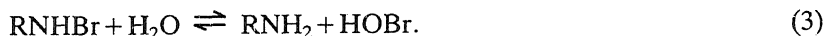
$k' \times 10^4 \text{ s}^{-1}$		
pH	BAB	BAT
5.0	9.70	8.84
5.5	7.42	7.20
5.7	5.83	6.11
6.0	4.17	4.27
6.2	2.70	3.13

Table 4. Kinetic and thermodynamic parameters for the oxidation of EDTA by BAB and BAT in acetate buffer of pH 5.

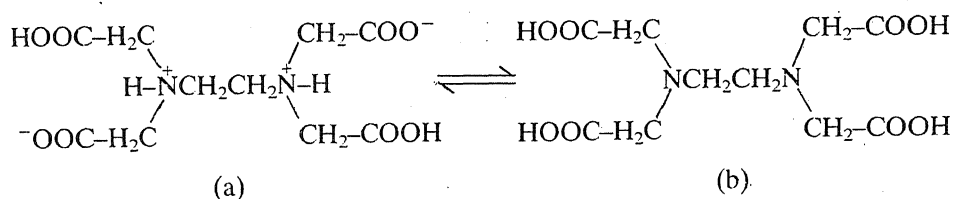
	E_a kJ mol ⁻¹	$\Delta H^\ddagger$ kJ mol ⁻¹	$\Delta S^\ddagger$ JK mol ⁻¹	$\Delta G^\ddagger$ kJ mol ⁻¹	log <i>A</i>
BAB	79.5	76.9	-48.8	92.0	12.0
BAT	90.2	87.7	-14.5	92.1	13.0

4. Discussion

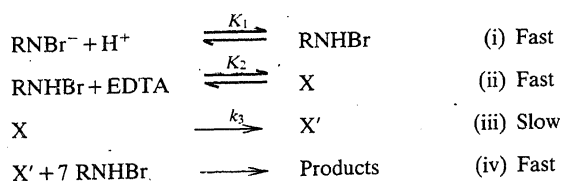
Investigations of Pryde and Soper (1926, 1931), Morris *et al* (1948) and Bishop and Jennings (1958) have established the nature of equilibria present in acidified chloramine-T solutions. The bromamine (BAB or BAT) is analogous to chloramine-T in its properties and in acid solutions the probable oxidizing species are the free acid RNHBr, dibromamine (RNBr₂) and HOBr. At pH > 4, the dibromamine does not exist in appreciable quantities. If HOBr is the active species, then a first order retardation by the added sulphonamide should have been observed (3).



Absence of a retardation effect by the sulphonamide rules out the involvement of HOBr in the reaction sequence. Bishop and Jennings (1958) have shown in their studies on aqueous solutions of CAT, that at pH > 3, the concentration of anion RNCl⁻ is greater than that of the free acid. Hence a protonation equilibrium (2) involving the anion can be assumed in aqueous solutions of RNBr Na in acetate buffer. EDTA can exist (Vogel 1978) in the form of a zwitterion (a) or as a neutral molecule (b).



Assuming that the substrate is in the neutral form, scheme 1 can be proposed for the oxidation of EDTA with BAB or BAT.



If $[\text{RNBr Na}]_t$ represents the total concentration of oxidant, then

$$[\text{RNBr Na}]_t = [\text{RNBr}^-] + [\text{RNHBr}] + [\text{X}],$$

for which rate law (4) can be derived.

$$-\frac{d[\text{RNBr Na}]}{dt} = \frac{k_3 K_1 K_2 [\text{RNBr Na}]_t [\text{EDTA}][\text{H}^+]}{1 + K_1[\text{H}^+] + K_1 K_2 [\text{EDTA}][\text{H}^+]} \quad (4)$$

Rate law (4) is in agreement with experimental results, where a first-order dependence on $[\text{RNBr Na}]$ and fractional orders in $[\text{substrate}]$ and $[\text{H}^+]$ were observed. Equation (4) can be transformed into (5) and (6).

$$\frac{1}{k'} = \frac{1}{k_3 K_2 [\text{EDTA}]} \left\{ 1 + \frac{1}{K_1 [\text{H}^+]} \right\} + \frac{1}{k_3}, \quad (5)$$

$$\frac{1}{k'} = \frac{1}{[\text{H}^+]} \left\{ \frac{1}{k_3 K_1 K_2 [\text{EDTA}]} \right\} + \left\{ \frac{1}{k_3 K_2 [\text{EDTA}]} + \frac{1}{k_3} \right\}. \quad (6)$$

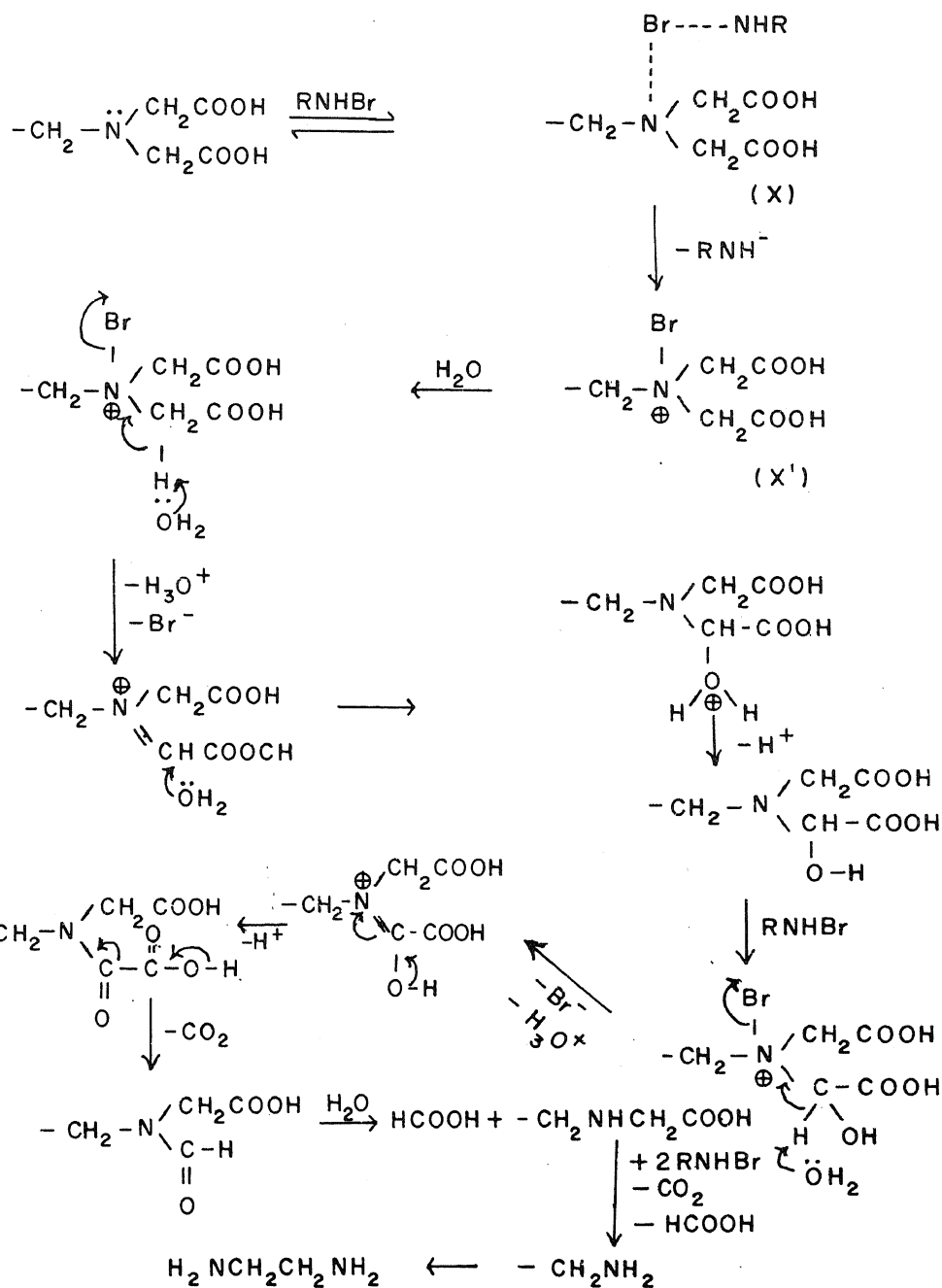
From the linear double reciprocal plots of $1/k'$ versus $1/[\text{EDTA}]$ ($r > 0.9978$) and $1/k'$ versus $1/[\text{H}^+]$ ($r > 0.9957$) values of decomposition constant k_3 , formation constant K_2 and protonation constant K_1 can be calculated. It may be noted that values of K_1 can be calculated both from (5) and (6). The results are shown in table 5. The value of K_1 obtained for BAB compares favourably with the value of 0.7×10^5 at 25°C found by Hardy and Johnston (1973). The formation constants of EDTA-oxidant complex are around 40, while the decomposition constants are $2.72 \pm 0.17 \times 10^{-3} \text{ s}^{-1}$.

The positive dielectric effect indicates charge dispersal in the transition state (scheme 1). The moderate ΔH^* and the large negative ΔS^* values support a rigid transition state. The mechanism of oxidation of EDTA by BAB and BAT envisages an electrophilic attack by the positive halogen of oxidant at the neutral nitrogen which subsequently leads to disruption of the substrate molecule, as explained in scheme 2.

Table 5. Values of protonation, decomposition and formation constants of EDTA-BAB or BAT complexes at 30°C , determined from double reciprocal plots.

	$10^{-5} K_1$ ($\text{dm}^3 \text{ mol}^{-1}$)		K_2 ($\text{dm}^3 \text{ mol}^{-1}$)	$10^3 k_3$ (s^{-1})
	<i>a</i>	<i>b</i>		
BAB	2.36	2.59	37.9	2.89
BAT	4.32	4.10	34.5	2.55

^a Values of K_1 calculated from (5); ^b Values of K_1 calculated from (6).



Scheme 2.

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Electrochemical reduction of diazepam

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Abstract. The reduction of 7-chloro-1,3-dihydro-1-methyl-5-phenyl-2H-1,4-benzodiazepine-2-one at the dropping mercury electrode has been investigated. The process is diffusion controlled; furthermore, the reduction wave enables the quantitative determination of the drug both in acid and basic media. The reagent captures two electrons and two hydrogen ions. A disproportionation reaction of the hydrazo-compound takes place, and amines are the final reduction products.

Keywords. Diazepam; polarography; cyclic voltammetry.

1. Introduction

Diazepam (7-chloro-1,3-dihydro-1-methyl-5-phenyl-2H-1,4-benzodiazepine-2-one, trade names; *Valium*, *Vival* and *Stesolid*, among others), a psychotherapeutic agent extensively used as a tranquilizer (Kales and Sharf 1973; Haider 1968; Matthew *et al* 1969), is also employed as an anticonvulsive in epileptic states (Browne and Penry 1973) due to its cardiovascular effects (Rao *et al* 1973). Because of its pharmacologic importance several procedures have been outlined for the determination of the presence of the drug in different materials by chromatography (De Silva *et al* 1964), spectrophotometry (De Silva *et al* 1966) and polarography (Oelschlager *et al* 1964; Barret *et al* 1973). The particular advantage of the last method is that the analysis can be carried out in the presence of the products of acid hydrolysis. As in many other medicines its action is closely related to oxidation-reduction mechanisms. Thus the electrochemical character of the polarographic study can greatly help obtain additional information.

The polarographic activity of the 1,4-benzodiazepines has been extensively reported. Senkowski *et al* (1964) investigated the polarographic behaviour of diazepam and Oelschlager (1963) compiled data on the related compound chlordiazepoxide hydrochloride. The reduction mechanism of oxazepam (Delschlager *et al* 1970) and nitrazepam (Halvorsen and Jacobsen 1972) have been also reported, as well as other benzodiazepines. Various assays have been developed for the analysis of chlordiazepoxide, diazepam, oxazepam, medazepam, nitrazepam, bromazepam, clonazepam, flunitrazepam and clorazepam in both biological samples and pharmaceutical dosage forms (Brooks *et al* 1975).

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It is the purpose of this paper to complete the study of the reduction reaction of diazepam by conventional and oscillographic polarography, and voltammetric and coulometric techniques in order to elucidate its electrochemical behaviour.

2. Experimental

The diazepam was supplied by IMPEX Quimica.

Direct current polarography: Tacussel and PO4 Radiometer. Electrodes: SCE, DME ($m = 2.2 \text{ mg sec}^{-1}$; $t = 3.92 \text{ sec}$), and a platinum wire.

Oscillographic polarography: Chemtrix SSP-3; SCE and dropping mercury electrode.

Cyclic voltammetry and coulometry: Amel-471. Electrodes used: SCE, working electrode for the cyclic voltammetry E410 Metrohm mercury hanging drop electrode. Controlled potential studies were carried out with a large stirred mercury pool electrode. In all the experiments the oxygen was removed by bubbling nitrogen gas (99.998% purity) through the solution. Britton-Robinson (B-R) buffers were used as supporting electrolyte solutions.

Since Cimbara and Gupta (1965) showed that the drug decomposed in aqueous solutions, we have dissolved the drug in methanol 20%/H₂O. Decomposition was negligible in this solvent. Therefore methanol-water mixtures have been used throughout. The polarographic measurements were done using a thermostated AMEL 494 cell. In all cases the temperature was maintained at $25.0 \pm 0.1^\circ\text{C}$.

3. Results and discussion

3.1. D.C. Polarography

The diazepam reduced at the dropping mercury electrode produces a polarographic wave at different concentrations, temperature and pH values. Figure 1 shows a representative polarogram at pH = 1.81, and the half-wave potential is $E_{1/2} = -0.705 \text{ V}$.

Examination of the electrocapillary curves (figure 2), obtained for 10^{-3} M diazepam and supporting electrolyte (B-R buffer, pH = 1.81) solutions, shows a great reduction of the drop time at the reduction potential. Based on this fact we can deduce that the drug is surface-active and is strongly absorbed on the dropping mercury electrode surface.

The effect of the drop time on the limiting current was analyzed by recording polarograms of $5 \times 10^{-4} \text{ M}$ diazepam in B-R buffer and 20% methanol at pH = 1.81 and 11.70, at various heights ($h_{\text{corr.}}$) of the mercury column. Plots of the limiting current values (i) against height were linear for both media, and the $i \times h^{-1/2}$ value remained constant. The temperature coefficient (determined in the range 5–35°C of the d.c. current) was 1.85% per degree. All these observations indicated that the polarographic wave under the conditions described is attributable to a process mainly controlled by the electroactive substance diffusing from the solution bulk to the dropping mercury electrode surface.

The effect of pH on the intensity-potential curves was also determined. The

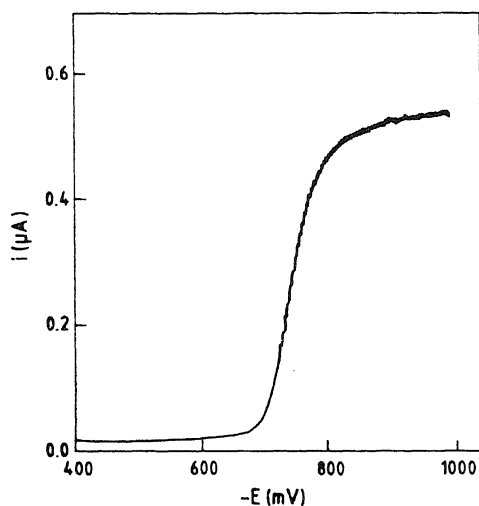


Figure 1. Polarogram of 5×10^{-4} M of diazepam dissolved in B-R buffer-methanol 20%, pH = 1.81.

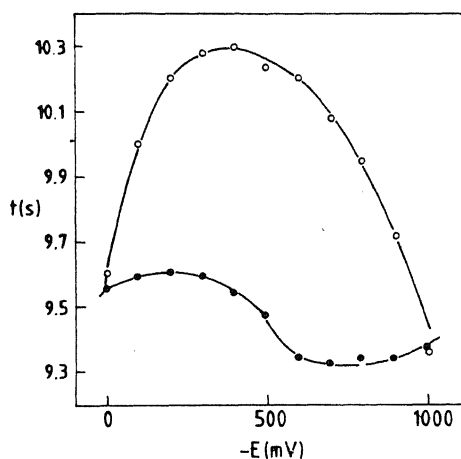


Figure 2. (-●-) Electrocapillary curve of 10^{-3} M diazepam in B-R buffer methanol 20%, pH = 1.81. (-O-) Electrocapillary curve of supporting electrolyte in B-R buffer, pH = 1.81.

half-wave potential shifts towards more negative values with an increase in electrolyte pH value indicating that hydrogen ions are consumed in the electrode reaction. There is a linear relation between both E magnitudes, and the half-wave potential, $E_{1/2} = -0.580, -0.060$ mV, in the pH range 1.81–11.88. The number of hydrogen ions, Z , involved in the electrode process is given by

$$E_{1/2}/\Delta\text{pH} = -0.059 Z/\alpha n_a,$$

where α is the transfer coefficient and n_a the number of electrons in the rate-controlling step of the reduction process. For the range of pH studied the αn_a

value calculated was 1.95 and the number of hydrogen ions was 1.85, indicating that two hydrogen ions are consumed in the global process.

The plots of the intensity values deduced from the diazepam polarograms at acidic (1.81) and basic (11.7) pH values versus concentrations of the active substance were linear in the 10^{-3} – 2.5×10^{-6} M range. The diffusion current constant (I) was $2.57 \mu\text{A l mmole}^{-1} \text{mg}^{-3/2} \text{sec}^{1/2}$. This value of I agrees with previously published values of similar compounds (Senkowski 1964).

3.2 Coulometry

The coulometric reduction at controlled potential diazepam in B-R buffer, pH 1.81, and methanol 20% was also studied. The pool mercury (used as working electrode) was maintained at -0.9 V potential. The samples contained 5×10^{-5} moles of diazepam in 50 ml of solution. It appears that the reduction involves 2.01 ± 0.04 electrons, so that it can be considered as a bielectronic process.

3.3 Cyclic voltammetry

The cyclic electrode voltammetric curves were recorded at different scan rates (figure 3). They always show a single cathodic wave, and the anodic peak resulting from reoxidation of the reduction product is absent. The shape of the cyclic voltammetry curve is in agreement with the diagnostic criteria proposed for systems in which an irreversible chemical reaction follows a reversible charge transfer (EC mechanism) (Wopschall and Shain 1967).

Voltammetric studies to evaluate the electrode reaction order and the electronic transfer coefficient were registered at different concentrations in the range of

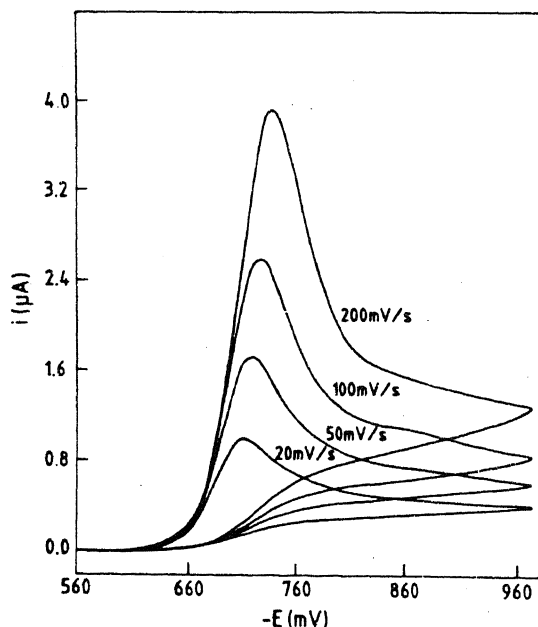


Figure 3. Cyclic voltammetric curves of 3×10^{-4} M, diazepam in B-R buffer-methanol 20%, pH = 1.81.

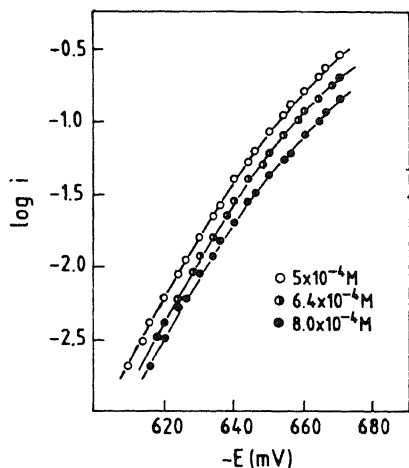


Figure 4. Representation of Tafel's equation for different reagent concentrations of diazepam.

10^{-4} M. The transfer coefficient determined from Tafel's slope (figure 4) is 1.32. Plots of $\log i$ values at -0.620 V versus the $\log$ -concentration C show a linear relation. Therefore the electrode reaction order with respect to the concentration is:

$$a = \left(\frac{\partial \log i}{\partial \log C} \right)_E = 1$$

Voltammograms of diazepam at different concentrations in the range $10^{-3} - 4 \times 10^{-6}$ M as a function of the potential scan rate allowed us to deduce the function current $i_p/Cv^{1/2}$ values. In figure 5 the current function variations versus scan rate, for several concentrations of the active substance, show dependence on both factors. However, this magnitude approaches a constant "diffusion controlled" value at slow scan rates and high bulk concentrations. This is a characteristic feature for surface-active depolarizers (Wopschall and Shain 1967). At fast scan rates adsorption prevails over diffusion, but if the solution concentration increases, the influence of adsorption decreases.

3.4 Oscillographic polarography

The oscillograms of 5×10^{-4} M diazepam, methanol 20% and B-R buffer at $\text{pH} = 1.81$ were recorded at different scan rates in the range between 0.5 and 10.0 V sec^{-1} . The dependence of the peak current on the square root of the scan rate of voltage can be considered as linear in the interval considered above. Extrapolation of the linear relationship does not however lead to zero current at zero voltage, but this fact has been attributed to the irreversibility of the electrode process (Delahay 1950).

Diazepam produces only one oscillographic cathodic wave confirming the character of the irreversible process according to the asymmetry observed between cathodic and anodic waves.

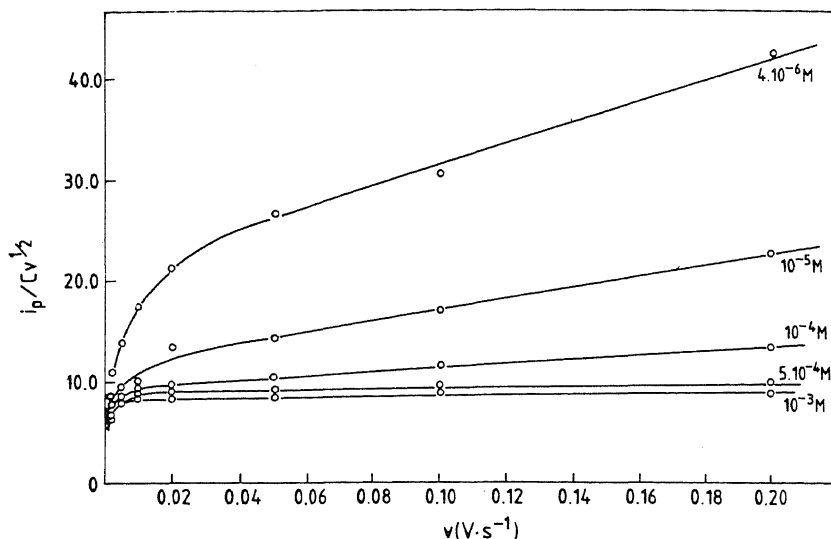


Figure 5. Current function variations versus scan rate for several concentrations of the active substance diazepam.

The dependence of the peak current on the diazepam concentration ($10^{-3} - 10^{-6} M$) was also studied. The shape of the wave is similar to other organic substances like phenazine (Laviron 1974) which were adsorbed on the mercury drop.

The non-zero intersection point with the coordinate axis obtained by data extrapolation suggests that at $1.7 \times 10^{-4} M$ concentration of diazepam, the electrode surface can be considered to be completely covered by a monolayer of the reaction product.

Laviron (1974) established that the interaction increases between the molecules adsorbed on the electrode surface, describing the adsorption by a certain isotherm, so that experimental features such as shifts on δ (peak width at half its height) and the peak potential (E_p), at the electroactive substance concentration, could be explained. In our case, the δ values increase with diazepam concentration, indicating that the predominance of repulsion over attraction increases between the molecules adsorbed on the surface of the mercury electrode.

The reduction peak of diazepam is well defined under the experimental conditions previously described. This may allow the quantitative determination of diazepam if the calibration curve has been established previously.

3.5 Current-time curves

Current-time curves were recorded at different potential values (-0.65 and $-0.90 V$). We observed that the polarographic curve of diazepam lay somewhere between them. The logarithmic analysis of the current-time curves clearly shows a linear shape. In our case, the examination of the $\log i$ versus $\log t$ plot allows us to estimate the β coefficient shift in the relation $i = k.t^\beta$, confirming the irreversible character of the electrode process.

4. Identification of the reduction products

In order to identify the reduction products, 50 mg of diazepam were electrolysed under the experimental conditions stated in §3.2. The system was extracted with Cl_3CH in a basic medium. The crude obtained was treated by column chromatography (2:3 hexane-ether), and 44 mg of a white powder was isolated.

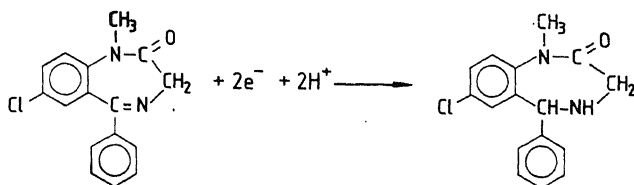
IR-The main fact observed is the appearance of a band at $3,311\text{ cm}^{-1}$ attributable to $\delta_{\text{N-H}}$ as well as the disappearance of $\delta_{\text{C=N}}$ at $1,650\text{ cm}^{-1}$ observed in the IR spectrum of diazepam.

$^1\text{H-NMR}$ (CDCl_3): 2.70 ppm (s_{broad} , 1H; proton exchangeable with D_2O), 3.32 (s , 3H), 3.41 (s , 1H) 5.22 (s , 1H), 6.72 (d , 1H, $J=2.0\text{ Hz}$), 6.95–7.95 (m , 8H).

The spectroscopic properties as well as the elemental analysis proved that the reduction product of the diazepam is the 4-5 dihydro-diazepam. This results confirm the hypothesis proposed by Cimbara and Gupta (1965).

5. Conclusions

The experiments carried out show that the 7-chloro-1,3-dihydro-1-methyl-5-phenyl-2H-1,4-benzodiazepine-2-one is reduced at the dropping mercury electrode; the reagent captures two electrons and two hydrogen ions. The only polarographic wave observed is due to a reduction of the azomethine group according to the following scheme:



Evidence of adsorption of the diazepam molecules on the electrode surface is, sustained by a study of the electrocapillary curves, and of the current function variation against the scan rate of potential by cyclic voltammetry, and also the oscillographic analysis as a function of the electroactive substance concentration. Further, the reduction wave enables the quantitative determination of the drug in the range of $2.5 \times 10^{-6} - 10^{-3}\text{ M}$ both in acid and basic media.

Acknowledgements

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Crystal structure of benzocaine—a local anaesthetic⁺

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Abstract. The structure of the local anaesthetic benzocaine was solved by direct methods and refined to an R of 0.12 for 531 observed reflections. The packing of the molecule is stabilised by N—H...O hydrogen-bonds (2.97 Å). The alkyl chain attached to the benzene ring is in *trans-trans* conformation. The benzoic moiety shows a quinonoid character as found in some other local anaesthetics.

Keywords. Local anaesthetic; benzocaine; *trans-trans* conformation.

1. Introduction

Benzocaine is a local anaesthetic and is like procaine, a para-substituted amino benzoate ester. Its low solubility renders it unsuitable for injections but its slow absorption from mucous-lined surfaces makes it safer than other local anaesthetics for ulcers and wounds. Though the anaesthesia produced is not so complete as with other local anaesthetics, it has been used topically with considerable success. Besides, the structure and conformational analysis of benzocaine would be of interest as that of a local anaesthetic of the ester type without a tertiary amino nitrogen.

2. Experimental

Colourless needles elongated along the a axis were readily obtained from a saturated solution of the compound in ethanol. The cell parameters are $a = 5.302$ (2), $b = 8.217$ (1), $c = 20.87$ (2) Å and space group $P2_12_12_1$ with $Z = 4$, $C_9H_{11}NO_2$, $M_r = 165.2$, $F(000) = 342$, $D_m = 1.21$ (1), $D_c = 1.218$ Mgm⁻³, $\lambda(\text{MoK}_\alpha) = 0.7093$ Å, $\mu = 0.9214$ cm⁻¹. The accurate values of the cell parameters were obtained by least squares refinement of measured angle values for 24 reflections in the range $45^\circ \leq 2\theta \leq 55^\circ$. A crystal of size $0.2 \times 0.3 \times 0.4$ mm was used for data collection on an automatic four circle CAD4 diffractometer with monochromatised MoK $_\alpha$ radiation ($\lambda = 0.7093$ Å) and $\theta/2\theta$ scan mode. The intensities recorded were very weak due to the poor quality of the crystal.

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⁺ DCB contribution No. 699

Repeated attempts at crystallisation under various conditions failed and the structure determination was carried out with the available data though the accuracy of the structure is limited. Out of a total of 803 reflections recorded, 700 were unique and 531 reflections with $I_{\text{net}} \geq \sigma(I_{\text{net}})$ were considered observed. These reflections were corrected for Lorentz and polarisation factors but not for absorption.

The structure was solved using the program MULTAN 80 (Main *et al* 1980). An initial model obtained from an E Map based on the best phase set failed to refine beyond $R = 0.20$. Hence, this model was assumed to be correctly oriented and was used in the phase refinement procedure (Karle 1968) of program MULTAN 80. The phase set having the highest figure of merit and lowest residual revealed all the non-hydrogen atoms. A few cycles of block diagonal refinement (Shiono 1968) with isotropic thermal parameters reduced the R -factor to 0.18. Hydrogens located from the difference fourier map were included in the last cycles of refinement, in the full matrix least squares procedure using the program LALS (Gantzel *et al* 1961). The final $R = 0.12$ Hughes weighting scheme with $F_{\text{o min}} = 7.3$ was used in the refinement (Hughes 1941).

$$W = (1/\sigma^2), \sigma = |F_0| \text{ if } |F_0| \geq |F_0|_{\text{min}} \\ = |F_0|_{\text{min}} \text{ if } |F_0| < |F_0|_{\text{min}}.$$

During the final cycle of refinement, $(\Delta/\sigma)_{\text{max}} = 1.0$ and $(\Delta/\sigma)_{\text{mean}} = 0.3$. The atomic scattering factors were taken from the International Tables for X-ray crystallography (1962). The final positional and thermal parameters of the non-hydrogen atoms are listed in table 1.

3. Discussion

Figure 1 shows a stereo-view of the molecule. Benzocaine is structurally similar to procaine and has many features in common. But there are several significant

Table 1a. Fractional atomic parameters for the non-hydrogen atoms ($\times 10^4$) and equivalent temperature factors with c.s.d. in parentheses.

$$B_{\text{eq}} = \frac{4}{3}(b_{11}a^2 + b_{22}b^2 + b_{33}c^2)$$

Atom	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
C(1)	2131(30)	848(21)	669(6)	5.74
C(2)	1229(25)	-648(21)	488(5)	4.40
C(3)	1934(30)	-2130(18)	700(6)	4.10
C(4)	3985(33)	-2249(16)	1092(6)	4.05
C(5)	5119(30)	-799(19)	1267(7)	4.40
C(6)	4381(33)	636(20)	1057(7)	4.60
C(7)	4874(20)	-3788(16)	1292(5)	2.69
C(8)	7882(43)	-5187(24)	1971(8)	6.43
C(9)	9831(35)	-4838(21)	2455(8)	5.80
N	1357(28)	2297(14)	431(6)	5.28
O(1)	6717(21)	-3706(12)	1731(4)	4.78
O(2)	4008(26)	-5047(11)	1125(5)	5.50

Table 1b. Anisotropic thermal parameters ($\times 10^3$) for the non-hydrogen atoms with e.s.d. in parentheses.

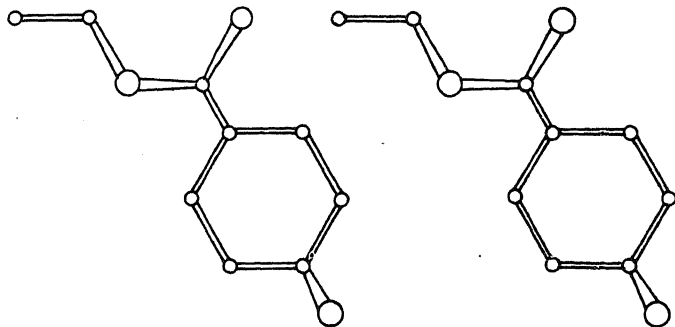
Atom	b_{11}	b_{22}	$*b_{33}$	b_{12}	b_{13}	b_{23}
C(1)	50(7)	30(3)	2(0)	5(9)	7(3)	1(2)
C(2)	27(5)	41(3)	2(0)	18(8)	-3(2)	6(2)
C(3)	49(7)	21(3)	3(0)	26(8)	-3(3)	2(2)
C(4)	52(8)	19(2)	3(0)	-6(8)	5(3)	2(2)
C(5)	50(7)	25(3)	3(0)	6(9)	8(3)	4(2)
C(6)	57(8)	25(3)	3(0)	-41(8)	-2(3)	-2(2)
C(7)	19(4)	19(2)	2(0)	-9(6)	-3(2)	-2(1)
C(8)	85(10)	34(4)	4(0)	-2(12)	-10(4)	8(2)
C(9)	47(7)	34(4)	5(0)	1(9)	-6(3)	11(2)
N	48(6)	26(2)	5(0)	19(7)	-5(3)	3(2)
O(1)	48(4)	25(2)	4(0)	-3(5)	-10(2)	1(2)
O(2)	70(6)	20(2)	5(0)	0(6)	-18(3)	-2(1)

*e.s.d.'s for b_{33} are less than 0.0005

$$T = \exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$$

Table 1c. Fractional coordinates ($\times 10^3$) of the hydrogen atoms and isotropic thermal factors with e.s.d. in parentheses.

Atom	x	y	z	$B_{\text{iso}}(\text{\AA}^2)$
HC(2)	48(31)	-59(17)	14(6)	1.68
HC(3)	79(31)	-30(17)	59(7)	3.27
HC(5)	607(32)	-106(17)	156(7)	4.51
HC(6)	482(34)	158(16)	115(6)	3.10
HC(8)1	661(37)	-605(20)	221(8)	0.08
HC(8)2	817(38)	-588(20)	156(7)	13.05
HC(9)1	857(32)	-428(18)	283(7)	11.11
HC(9)2	1087(32)	-561(17)	266(7)	5.92
HC(9)3	1120(32)	-398(17)	228(7)	8.22
HN(1)1	-18(34)	224(18)	24(7)	8.87
HN(1)2	189(34)	298(17)	62(7)	6.49

**Figure 1.** Stereo view of the molecule.

differences observed between them. The benzoic moiety is planar in procaine (Sinha *et al* 1984; Kashino *et al* 1982) and its nitrophenyl phosphate complex (Sax *et al* 1970). But in the present structure the phenyl ring is non-planar ($\chi^2 = 45.3$). The atom O(1) of the ether group deviates from the least squares plane through the phenyl ring by ($-0.12\text{\AA}$). Similar deviations have been observed in the *bis-p*-nitrophenyl complex of benzocaine (Pletcher *et al* 1972). Such a non-planarity has been ascribed to 'small conformational changes in the alkyl chain (Sax *et al* 1971). The torsion angle about the ester bond is $-178(1)^\circ$ which is close to the value found in nitrophenyl phosphate complex of procaine [$178.1(4)^\circ$], but differs significantly from that in the benzocaine complex [$-168.6(2)^\circ$] and procaine [$147.1(4)^\circ$]. These conformational variations may be the result of packing and other steric requirements (Pletcher *et al* 1972) of these molecules. The rotation of the carbonyl group about the C(4)–C(7) bond is $3(2)^\circ$ as compared to 9.4° (7) in the benzocaine complex and 2.5° (6) in the procaine complex and $-2.0(6)^\circ$ in procaine.

The para-substituted amino group is unprotonated and the benzoic moiety exhibits a quinonoid character as in procaine. The bond lengths and bond angles in the benzene ring indicate significant contribution of this character as is evident from the fact that C(1)–C(2) and C(1)–C(6) bonds are longer than the C(2)–C(3) and C(6)–C(5) bonds, and also the angles C(2)–C(1)–C(6) and C(3)–C(4)–C(5) are smaller than the other angles in the ring. The angle C(2)–C(1)–C(6) [$109(1)^\circ$] is significantly smaller than the corresponding angles observed in procaine [$118.1(3)^\circ$] and 2-amino-3-methyl benzoic acid [$118.8(2)^\circ$]. Such deformations may be due to the electron-releasing nature of the para-substituent (Domenicano *et al* 1975). The quinonoid character of the benzoic moiety has not been observed in the *p*-nitrophenyl phosphate complex of benzocaine and it has been explained as being the consequence of the protonation of the para-substituted amino nitrogen in the complex. In benzocaine and procaine, the quinonoid character can be ascribed to the conjugation of the amino nitrogen with the benzoic moiety down to the carbonyl group.

The C(1)–N(1) bond length [$1.35(2)\text{\AA}$] is significantly different from those observed in benzocaine complex [$1.464(9)\text{\AA}$], procaine [$1.458(8)\text{\AA}$] and amino phenyl hydrochloride (Cesur and Richards 1965) [$1.474(9)\text{\AA}$], but it is close to that observed in 2-amino 3-methyl benzoic acid [$1.37(1)\text{\AA}$] and this shortness has been ascribed to the hybridization effects (Brown and Marsh 1963). All other bond lengths and angles are comparable within experimental error to those in similar structures (figure 2).

Figure 3 shows the packing of the molecule down the *a* axis. The amino nitrogen is hydrogen-bonded to the carbonyl oxygen as in the structure of the benzocaine complex. The N–H...O hydrogen bond distance is $2.97(2)\text{\AA}$ with the N–H...O angle $172(1)^\circ$ and the H...O distance $2.25\text{\AA}$.

Acknowledgement

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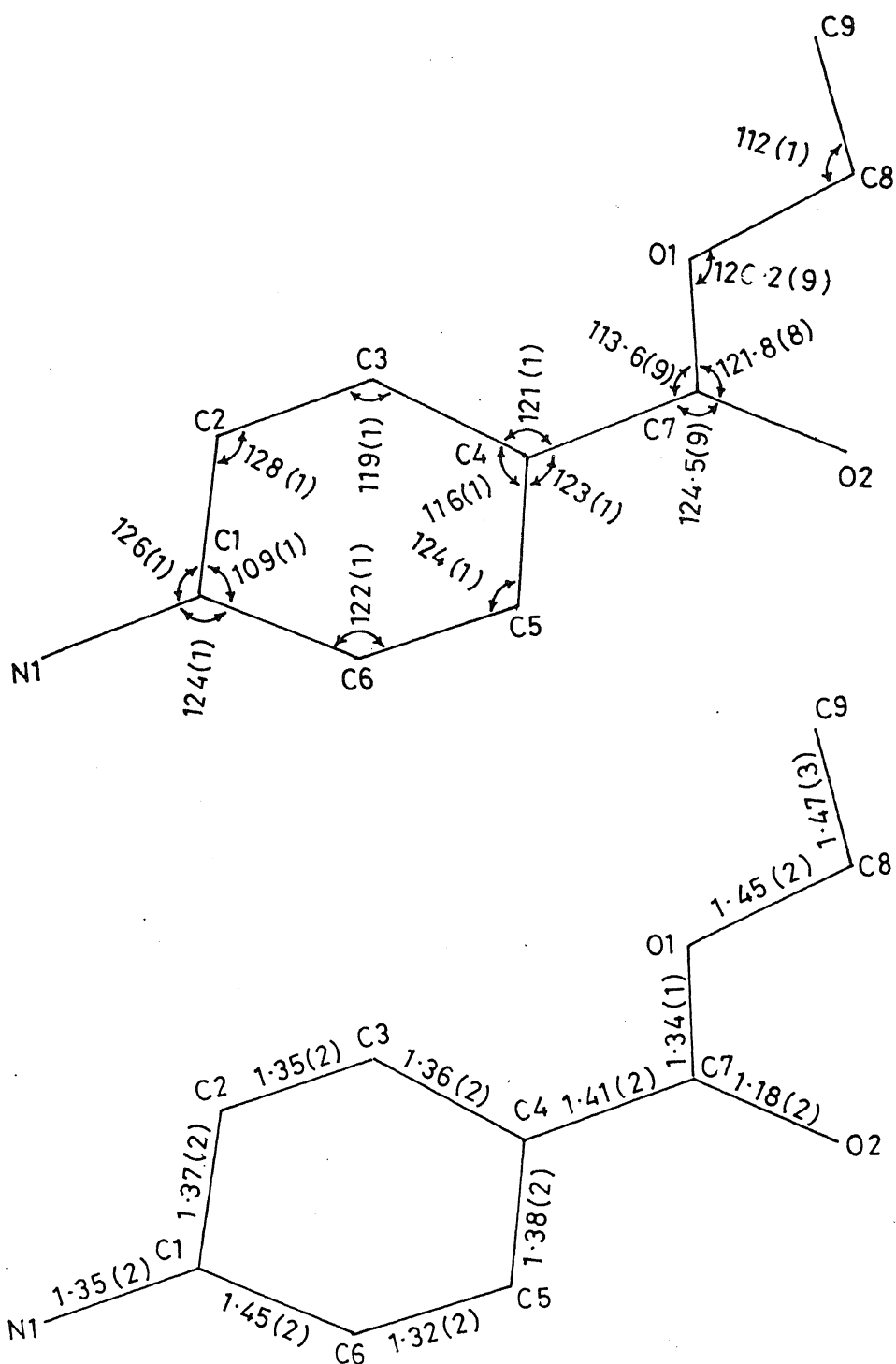


Figure 2. (a) Bond lengths (Å) with e.s.d. in parentheses. b. Bond angles (°) with e.s.d. in parentheses.

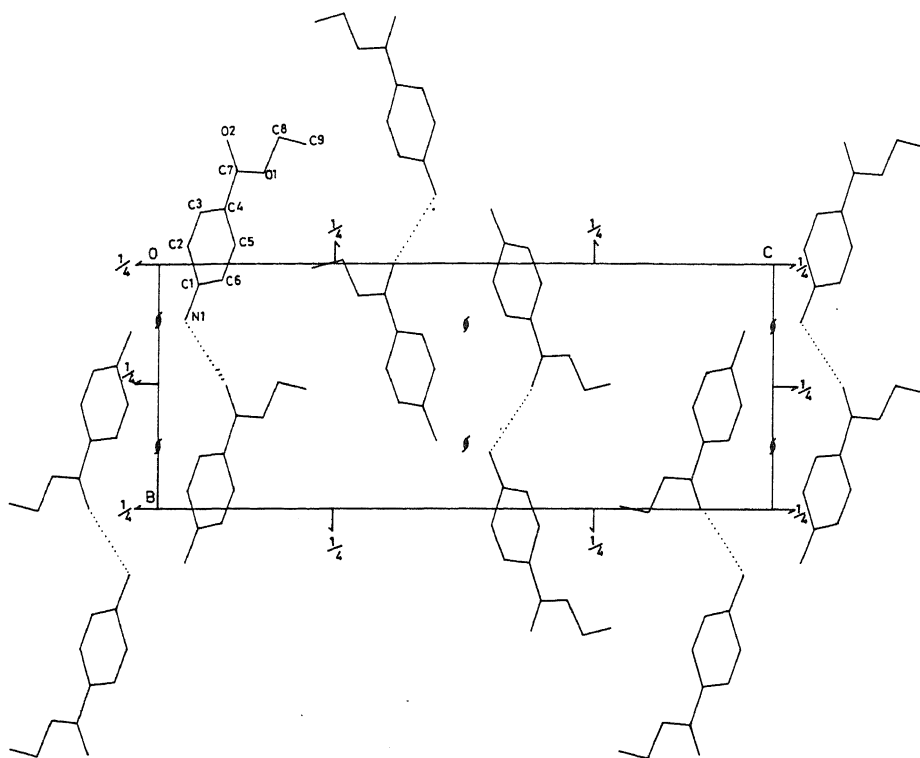


Figure 3. Packing of the molecule projected down the *a* axis. Hydrogen-bonds are indicated by dashed lines.

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The role of solvent models in stabilizing nonclassical ions

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Abstract. A molecular dynamics simulation is performed for a system of classical and nonclassical 2-norbornyl cations surrounded by a model solvent. Comparison of the energies of stabilization of the two ions due to the model solvent medium indicates that the difference in stabilization energies of the two ions is less than 1 kcal/mol.

Keywords. Molecular dynamics; classical and nonclassical ion controversy.

1. Introduction

To account for the difference between the exo and endo solvolysis of 2-norbornyl derivatives the nonclassical 2-norbornyl cation was postulated (see figure 1) (Winstein and Trifan 1952). The exo solvolytic rates were larger than the endo rates by factors of the order of 1000 (Goering and Schewene 1965). These rate differences lead to a difference in the activation free energies (ΔG) for the two reactions; the exo solvolysis having a ΔG around 6 kcal/mol smaller than the endo.

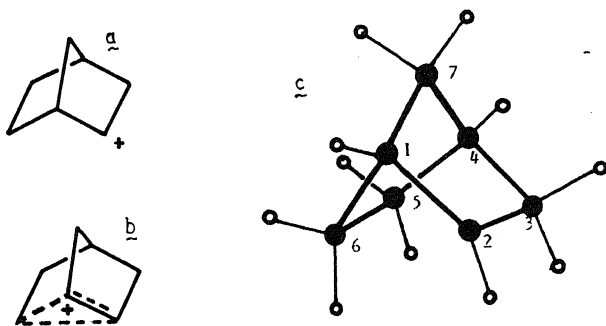


Figure 1. (a) Classical ion; (b) nonclassical ion; (c) geometry of classical ion: *Bond lengths* (Å) C1C2 (1.50), C1C6 (1.550), C1C7 (1.54), C6C5 (1.54), C2C3 (1.50), C5C4 (1.55), C3C4 (1.556), C4C7 (1.54). *Angles (degrees)* C1-C7-C4 (96.9), C7-C4-C3 (101.4), C7-C4-C5 (102.4), C5-C4-C3 (105.4), C7-C1-C2 (107.3), C7-C1-C6 (99.1), C6-C1-C2 (99.6), C4-C3-C2 (100.5), C4-C5-C6 (102.5), C1-C2-C3 (109.9), C1-C6-C5 (102.8). All other C-H lengths and H-C-H angles are same as in Goddard *et al* 1982.

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In order to account for this difference, several *ab initio* as well as semi-empirical quantum chemical calculations have been performed on the two isolated ions in the gas phase to see which one is more stable (Klopman 1969; Dewar *et al* 1977; Goetz *et al* 1977; Wenke and Lenoir 1979; Kohler and Lischka 1979; Goddard *et al* 1982; Raghavachari *et al* 1983; Yoshimine *et al* 1983). There is a considerable spread in the results obtained in these studies, no doubt due to the different levels of sophistication used in various calculations. In the above calculations the role of the solvent is not taken into account. To get an idea of the influence of the solvent, models of classical and nonclassical ethyl cations were surrounded by 5 HCl molecules and the classical ion was found to be preferentially stabilized by 16 kcal/mole (Jorgensen and Munroe 1977). The existence of a nonclassical structure for norbornyl cation was confirmed earlier by Olah and coworkers (for a review, see Olah *et al* 1983) and recently by Yannoni *et al* (1982) and Myhre *et al* (1985) by spectroscopic measurements. However, Brown (1983, 1986) questions the arguments supporting the nonclassical structure based on various experimental factors and Schleyer has critically examined Brown's arguments (Brown 1977). In the study of the solvation of the 2-norbornyl cation one has to have detailed knowledge of the nature of the interactions between the ion and the solvent molecules, and also among the solvent molecules themselves, and perform a statistical averaging over all possible solvent configurations around the ions. If the solvent molecules are dipoles or charged species, they will contribute significantly to ionic solvation. One may also like to consider the contribution from different solvation shells around the ions to the energy of solvation.

In a Monte Carlo simulation of the relative solvation of parallel and perpendicular allyl cations in a strongly hydrogen-bonding solvent (liquid HF), Jorgensen and coworkers found that the parallel allyl cation is strongly hydrogen-bonded to two HF molecules (Cournoyer and Jorgensen 1984). The solvent contribution to stabilization was greater in the case of the perpendicular form than in the parallel form by 25 kcal/mol. The potential functions used in the calculations were obtained by *ab initio* calculations using a 4-31G basis set. Recent semi-empirical quantum calculations support the suggestion that the 2-norbornyl cation is a "nonclassical-classical" carbo cation (Dewar and Merz 1986). In our present work, we are exploring the changes in the solvation energies due to bridging, which has been postulated for the nonclassical 2-norbornyl cation. The model potentials and the method of calculation are discussed in the next section. This is followed by results and discussion.

2. Method

Our model represents the ions in a weakly ionic/dipolar low density solvent. The system is contained in a spherical cell of radius 8 Å with the cation (solute) held fixed at the centre of the cell (Tembe and McCammon 1984). The coordinates of the ions are based on the data of Chiang *et al* (1968) and Goddard *et al* (1982). We have focussed our attention on the charge on the second carbon (C2), which is localized in the classical case and delocalized in the nonclassical case. In the nonclassical ion the only change that is made is in the distribution of the excess charge. The ions are surrounded by 28 model solvent particles. The system density

is about half of the density at closest packing.

The interaction potential for particles i and j separated by a distance r is given by

$$U_{ij}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] + q_i q_j / r, \quad (1)$$

where the first term is the Lennard-Jones potential function with the parameters $\epsilon/k = 120$ K and $\sigma = 3.4$ Å representing the interaction between spherical particles at locations i and j , and q_i and q_j the charges on particles i and j , respectively. The actual interaction potential between the norbornyl ion and solvent are not available and even the interactions between simple ions like Li^+ and Na^+ with polar solvents like water are becoming available only in the last few years (Rossky 1985). In this work we are taking into account the dominant interactions between the ion and the solvent by the most common empirical potentials. The charge-charge interactions used here are on the average greater than the charge dipole interactions which decay as $1/r^3$ and our results could be slight overestimates of the solvent contribution to stabilization. In simulation A the value of σ was the same between all pairs of atoms. In simulation B the value of σ was 3.4 Å for all pairs except for the solvent and the hydrogen atoms on the solute ion. This latter value of σ was taken to be 2.07 Å. The solvent particles have charges of $\pm 0.1e$, where e is the electronic charge. This is equivalent to a charge of $1e$ on C2 in a medium of dielectric constant of 10. The C and H atoms of the cation interact with the solvent particles only via the Lennard-Jones interaction except that in case of the classical cation the centre C2 has a charge of $q_2 = 0.1e$ and the electrostatic part of the interaction is given by

$$U_s^C = \sum_{s=1}^{28} q_2 q_s / r_{2s}, \quad (2)$$

where q_s is the charge on the solvent particle and r_{2s} is the distance between C2 and the solvent particle s . In the nonclassical ion the positive charge at C2 is distributed on a triangle formed between carbons 1, 2, and 6. We have distributed 18 point charges on the triangle such that the total charge is the same as the charge on the classical cation ($q_2 = 0.1e$). On each of the three bonds C1C2, C2C6 and C6C1, one third of q_2 is spread uniformly. The electrostatic interaction with the solvent of the nonclassical ion is

$$U_s^N = \sum_{s=1}^{28} \sum_{i=1}^{18} q_n q_s / r_{is}, \quad (3)$$

where q_n is the charge on each of the 18 points on the triangle, r_{is} the distance between point i and the solvent particle s .

Using the potentials given above a molecular dynamics simulation is performed for the calculation of the energy of stabilization of the 2-norbornyl cation due to the solvent medium. Knowing the forces at each particle, new positions are calculated. This is achieved by numerically solving Newton's equations of motion. The time step for the simulation is 0.02 picoseconds. Stochastic boundary conditions are used wherein a uniform temperature is maintained by randomly reassigning velocities from a Maxwellian distribution at 298 K to 5 particles per time step. The particles are confined within the 8 Å cell by imposing a harmonic wall potential. We use the Verlet algorithm to integrate the equations of motion (Verlet 1967). In our present

studies we have focussed our attention on solute-solvent interaction energies. The system is allowed to equilibrate from a lattice configuration for the first 2000 steps of simulation. The average values of the solvent-solute and solvent-solvent interaction energies are calculated for the next 10,000 steps of simulation.

3. Results and discussion

In table 1 the results of our simulation are given. It is noticed that the difference in the solute-solvent interaction energies between the classical and nonclassical systems in simulation A is 0.15 kcal/mol. and in B it is 0.4 kcal/mol. As we change the closest distance of approach of the solvent particles up to the hydrogens of the two ions from 3.4 Å to 2.07 Å, the stabilization has changed by 0.15 to 0.4 kcal/mol. This implies that the small differences in C-C and C-H bond lengths between the classical and nonclassical ions (which are less than 2%) are going to make a significant difference in our results for the stabilization due to solvation. Thus these model calculations show that the contribution of the solvent to the preferential stabilization of either of the ions after statistical averaging is less than 1 kcal/mol. We are presently looking into the effect of system size as well as system density on the relative stabilization energies reported here. In a recent simulation by Engstrom *et al* (1984) it has been observed that the system size has a relatively small effect on the quadrupole relaxation of atomic ions. The simulation reported by us is analogous to a simulation where a charge of $1e$ is localized on C2 or spread around C2 in a medium of dielectric constant of 10 but a density smaller than the actual density used in experimental systems. We are investigating the influence of the variation of q_2 and the dielectric constant reported here but we do not expect the preferential stabilization due to bridging to be greater than the experimentally observed differences in ΔG in media with dielectric constants greater than 10.

Table 1. Average solvent-solvent and solute-solvent interaction energies in classical and nonclassical systems over 10,000 steps of simulation (200 ps).

Simulation A

	Solvent-solvent	Solute-solvent	Total
Classical ion	-1.104	-11.900	-13.004
Nonclassical ion	-1.097	-11.758	-12.855
Difference (nonclassical-classical)	0.007	0.142	0.149

Simulation B

	Solvent-Solvent	Solute-Solvent	Total
Classical ion	-1.158	-7.153	-8.311
Nonclassical ion	-1.171	-6.745	-7.916
Difference (nonclassical-classical)	-0.013	0.408	0.395

All computations were done using an IBM PC-XT; the classical ion took 15 minutes while the nonclassical ion 17 minutes for 100 steps of simulation. (All values in kcal/mole).

Our calculations indicate a ΔE of about 1 kcal/mol. in a non-hydrogen-bonding model solvent in contrast to Jorgensen's result of 25 kcal/mol for parallel and perpendicular allyl cations in liquid HF. The relative solvation of structures like parallel and perpendicular allyl cations and classical and nonclassical ethyl cations in our model solvent and models for solvents such as water, alcohol and 30% acetone will give us a clearer indication of the role of intermolecular interactions in solvation. The main route at present for obtaining the solute-solvent interaction energies is by the use of the molecular orbital method. Although there is no direct experimental method to verify these potentials in the condensed medium (as against the gas phase), results derived from these potentials will provide a quantitative answer to the relative magnitudes of solvation and also the detailed solvent particle distributions about the ions. As the solvation energies are derived from kinetic data it would be of great interest to investigate the structure and dynamics of the solvent particles when a leaving group such as tosylate or a halide ion is in the process of leaving from the exo and the endo positions. Calculations of potential energy surfaces between the ions and the solvent particles in a bulk medium or a condensed environment are being investigated quite actively by several investigators.

It may be of interest to compare the results obtained in this study with the results known for the electrostatic contribution to the solvation free energies of a spherical non-electrolyte solute molecule. The Born equation (Born 1920) for the solvation energy in a continuum dielectric is

$$G_{\text{sol}}^{\circ}(i) = [N(Z_i e)^2 / 2r_i] / (1 - 1/D). \quad (4)$$

In this expression r_i is the radius of the ion, Z_i is the valence of the ion, e the electronic charge, D the dielectric constant and N the Avagadro number. As the radius of the ion is decreased, the solvation energy increases. As the charges get confined to smaller volumes such as edges and pointed tips, the electric field around them increases dramatically and the medium around them is polarized further resulting in larger solvation energy. Thus when we go from classical to nonclassical ions, the solvation energy is expected to decrease due to a greater spread from the original point or spherical charge. In the problem studied in our model, let us suppose that the charge contained at C2 of the classical ion of radius r_i is distributed into 18 separated spheres of smaller radii such that the total volume of the droplets is equal to the original volume of the sphere. If we assume that these spherical droplets are independent, then the ratio of solvation energy of the classical to the nonclassical is given by $18^{2/3}$. In addition to the neglect of nonelectrostatic effects and the molecular nature of the solvent in the Born model, this calculation assumes that the charges in the nonclassical ion are separated beyond molecular distances. However, this gives an indication of the order of magnitude of results in a continuum model.

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Synthesis and spectroscopic studies of platinum (II) and palladium (II) complexes with amino acids and polypyridyl ligands

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Abstract. Ten amino acid complexes of platinum (II) and palladium (II) of the type $[M(L-L)(a-a)]Cl$ (where $M = Pt$ or Pd ; $L-L$ = bidentate polypyridyl chelating agents and $a-a$ = amino acids, S-methyl-L-cysteine or L-methionine) have been synthesized and characterized by various physical methods. The conductivity data show that these complexes are 1:1 electrolytes and confirm the above formation. The ultraviolet spectra of these complexes show $\pi-\pi^*$ bands of polypyridyl ligands and MLCT bands, while $d-d$ bands are obscured. The 1H NMR spectra of these complexes show that the amino acids are bonded to platinum and palladium through nitrogen and sulphur atoms. The infrared data have further supported the above bidentate mode of binding of the amino acids while the carboxylate group of the amino acids remains uncoordinated and deprotonated in these complexes. The S-methyl-L-cysteine complexes exist as diastereoisomers due to the presence of a chiral sulphur atom as identified by 1H NMR.

Keywords. Anticancer; intercalation; amino acid; DNA.

1. Introduction

A considerable number of metal complex compounds are now known to possess antitumour activity (Rosenberg 1971; Williams 1972; Cleare 1974). The most widely used clinically is the complex *cis*-dichlorodiamine platinum (II), cisplatin, which is thought to bind DNA *in vivo* (Rosenberg 1980). Recently some sulphur containing amino acid derivatives (Shohat *et al* 1972; Cheng *et al* 1972) and platinum complexes of sulphur containing amino acids and peptides were found to have inhibitory action against tumours (Zakharova *et al* 1981; Williams and Graham 1979; Mogilevkina *et al* 1979). Also, cationic platinum complexes $[Pt(2,2',2''-terpyridyl)(2-mercaptoethanol)]^{1+}$, $[Pt(2,2'-bipyridyl)(ethylene-diamine)]^{2+}$, $[Pt(2,2',2''-terpyridyl)(cysteine)]^{1+}$ were found to bind the double stranded DNA in an intercalative fashion and stabilize the stacked complexes by additional hydrogen-bonding between coordinated ligands such as 2-mercaptoethanol, ethylenediamine, cysteine and the phosphate backbone of DNA (Lippard 1978; Barton and Lippard 1980). Keeping the non-covalent interactions in the above and related systems in

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view, we have synthesized ternary platinum (II) and palladium (II) complexes with the general formula $[M(L-L)(a-a)]Cl$ where M = platinum (II), Pt or palladium (II), Pd; $L-L$ = 2,2'-bipyridyl (bpy), 1-10 phenanthroline (phen), 2,2'-dipyridylamine (dpa), and $a-a$ = amino acids, S-methyl-L-cysteine (MC) or L-methionine (M). In these amino acid complexes, the various types of non-covalent interactions such as hydrogen-bonding, ionic bonding and van der Waals' interactions between side chains of amino acids (Wood *et al* 1974) and phosphate backbone or nucleoside of DNA molecule are possible for stabilizing the stacked complexes.

2. Experimental

2.1 Materials

K_2PtCl_4 , K_2PdCl_4 , 2,2'-dipyridylamine and S-methyl-L-cysteine were purchased from Aldrich Chemical Company Inc., USA. 2,2'-bipyridyl, 1-10 phenanthroline and L-methionine were purchased from Sisco, India. All other chemicals used were reagent grade. Solvents were purified and dried prior to use.

2.2 Syntheses of the complexes

2.2a $M(L-L)Cl_2$ complexes: $Pt(bpy)Cl_2$ and $Pd(bpy)Cl_2$ were prepared according to known procedures (Palocsay and Rund 1969; McCormick *et al* 1971). $Pt(phen)Cl_2$, $Pd(phen)Cl_2$, $Pt(dpa)Cl_2$ and $Pd(dpa)Cl_2$ (A S Gijre and V N Joshi, unpublished results) were prepared by methods similar to those for $Pt(bpy)Cl_2$ and $Pd(bpy)Cl_2$. Their purities were checked by elemental analyses and spectral data.

2.2b $[M(L-L)(a-a)]Cl$: These complexes were prepared by a general procedure as follows. To a 0.1 mM suspension of the respective $M(L-L)Cl_2$ complex in 20 ml of methanol, a concentrated aqueous solution of sodium salt of the appropriate amino acid (0.1 mM) was added with constant stirring. The temperature of the reaction mixture was gradually raised to 60–65°C and stirring was continued to get a clear solution ($\sim$ 4 hours for palladium and $\sim$ 24 hours for platinum complexes). The resulting yellow-coloured solution was then filtered to remove unreacted $M(L-L)Cl_2$, if any, and concentrated on a water bath to 5–6 ml volume. On cooling the concentrated solution to room temperature a yellow product crystallized out. These crystals were filtered, washed with ice cold methanol and then with acetone. The compound was finally dried in vacuum over anhydrous calcium chloride for 8 hours. The yield was more than 70%.

2.3 Physical measurements

Carbon, hydrogen and nitrogen analyses were carried out using standard methods. Palladium was estimated gravimetrically as palladium dimethyl-glyoxime and platinum as metallic platinum (Vogel 1978).

Conductivity measurements were carried out on a 'Systronic conductivity bridge 305' using a conductivity cell with a cell constant of 0.59 in double-distilled water. Electronic adsorption spectra of these complexes were recorded on a Perkin-Elmer 402 uv-vis spectrophotometer in double-distilled water in the range 190 to 850 nm. Infrared spectra were recorded on a Pye-Unichem S-200 infrared spectrophoto-

meter in KBr pellets in the range 4000 to 200 cm^{-1} . ^1H NMR spectra were recorded on a Varian XL-100 NMR spectrometer in D_2O using DSS as the internal standard.

3. Results and discussion

Amino acid complexes of the type $[\text{M}(\text{L-L}) (\text{a-a})]\text{Cl}$, were prepared by the interaction of the respective $\text{M}(\text{L-L})\text{Cl}_2$ with the appropriate amount of the sodium salt of the amino acid in water-methanol mixture at $\sim 60^\circ\text{C}$. The reaction times were different for palladium and platinum as expected (Cotton and Wilkinson 1980). The above complexes were characterized by elemental analysis, conductivity measurements and uv-vis, IR and ^1H NMR spectroscopy.

The analytical and conductivity data of these complexes with their colours are given in table 1. The analytical data are in good agreement with the proposed formula $[\text{M}(\text{L-L}) (\text{a-a})]\text{Cl}$. The conductivity data are in accordance with the values for 1:1 electrolytes (Geary 1971). All the compounds are diamagnetic in nature.

The amino acid complexes of platinum and palladium show several absorption maxima. The positions of these band maxima and their molar extinction

Table 1. $[\text{M}(\text{L-L}) (\text{a-a})]\text{Cl}$ complexes with their colour, analytical and conductivity data.

Compound (Colour)	%C Calc. ^a (found)	% H Calc. (found)	% N Calc. (found)	%M ^b Calc. (found)	Conductivity of 10^{-3}M solution [$\text{cm}^2\text{ohm}^{-1}\text{mol}^{-1}$]
$[\text{Pt}(\text{bpy}) (\text{MC})]\text{Cl}$ (yellow)	32.27 (31.90)	3.07 (3.34)	8.06 (8.10)	37.46 (37.29)	88
$[\text{Pd}(\text{bpy}) (\text{MC})]\text{Cl}$ (yellow-orange)	38.93 (38.62)	3.70 (2.95)	9.73 (9.52)	24.56 (25.11)	102
$[\text{Pt}(\text{phen}) (\text{MC})]\text{Cl}$ (orange-red)	35.26 (34.80)	2.93 (3.24)	7.71 (8.18)	35.81 (36.00)	122
$[\text{Pd}(\text{phen}) (\text{MC})]\text{Cl}$ (yellow)	42.15 (42.36)	3.51 (4.09)	9.22 (9.50)	23.27 (23.51)	107
$[\text{Pt}(\text{dpa}) (\text{MC})]\text{Cl}$ (yellow)	31.37 (30.85)	3.17 (3.08)	10.45 (10.81)	36.41 (36.77)	126
$[\text{Pd}(\text{dpa}) (\text{MC})]\text{Cl}$ (yellow)	37.62 (37.56)	3.82 (4.31)	12.54 (12.44)	23.74 (23.26)	92
$[\text{Pt}(\text{phen}) (\text{M})]\text{Cl}$ (brownish-yellow)	36.52 (36.88)	3.22 (3.37)	7.52 (7.23)	34.91 (34.61)	107
$[\text{Pd}(\text{phen}) (\text{M})]\text{Cl}$ (brownish)	43.45 (43.13)	3.83 (4.23)	8.94 (8.79)	22.87 (22.10)	120
$[\text{Pt}(\text{dpa}) (\text{M})]\text{Cl}$ (yellow)	32.75 (33.01)	3.45 (3.80)	10.19 (10.45)	35.48 (34.83)	87
$[\text{Pd}(\text{dpa}) (\text{M})]\text{Cl}$ (yellow-orange)	39.08 (38.73)	4.12 (3.76)	12.16 (12.67)	23.01 (23.42)	130

^a Calc. is calculated; ^bM—metal, Pt or Pd.

Table 2. Electronic spectra of $[M(L-L)(a-a)]Cl$ complexes:

Compound	Band maximum in kK ^a				
	I	II	III	IV	V
[Pt(bpy) (MC)]Cl	27.76 (0.28) ^b	31.54, 32.67 (1.17) (0.93)	33.76sh ^c (0.57)	40.81 (1.42)	44.84
[Pd(bpy) (MC)]Cl	28.57 (0.36)	31.06, 32.89 (0.96) (1.28)		41.32 (1.58)	
[Pt(phen) (MC)]Cl	28.24, 29.32 (0.161) (0.21)		33.11 (0.95)	36.10 (2.6)	44.84 (3.2)
[Pd(phen) (MC)]Cl	27.10, 28.96 (0.20) (0.24)		33.00 (1.10)	36.32 (2.17)	44.73 (2.92)
[Pt(dpa) (MC)]Cl	28.36 (0.18)	30.16sh (0.39)	32.6br ^d (0.83)	41.58 (1.62)	
[Pd(dpa) (MC)]Cl	28.41 —	30.16sh (0.412)	32.78 (0.74)	40.40 (1.56)	
[Pt(phen) (M)]Cl	28.20, 29.27 (0.14) (0.22)		33.14 (0.78)	36.45 (2.18)	44.67 (3.12)
[Pd(phen) (M)]Cl	27.83, 28.67 (0.21) (0.24)		33.10 (0.83)	36.20 (2.02)	44.80 (3.43)
[Pt(dpa) (M)]Cl	28.40 —	30.12sh (0.32)	33.11br (0.78)	41.32 (1.40)	
[Pd(dpa) (M)]Cl	28.24 (0.15)	30.00sh (0.35)	33.78br (0.71)	40.48 (1.54)	

^a kK is $1 \times 10^{-3} \text{cm}^{-1}$.^b the extinction coefficients in $1 \text{ mol}^{-1} \text{ cm}^{-1} \times 10^{-4}$ are given in parenthesis.^c sh—shoulder;^d br—broad peak.

coefficients are given in table 2. The electronic absorption spectra of these amino acid complexes are similar to those of the corresponding $M(L-L)Cl_2$ complexes in band profile with slight changes in band positions and molar extinction coefficients. All the complexes show ligand $\pi \rightarrow \pi^*$ transitions. Additional strong bands which can be identified with lower molar extinction coefficient values than those for $\pi \rightarrow \pi^*$ transitions can be attributed to the metal to ligand charge transfer transitions (Possiolo 1967; A S Gijre and V N Joshi, unpublished results).

The 1H NMR spectra of these complexes have been recorded in D_2O . Table 3 lists the chemical shifts of H-6,6' protons of bpy or dpa and S-CH₃ and CH protons of amino acids. The $^{195}Pt-S-C-H$ and $^{195}Pt-N-C-H$ coupling constants [$^{195}Pt \sim 33\%$ abundance, $I = 1/2$] whenever observed are also given. The protons near the binding sites of amino acid (S, N) are shifted up- or down-field upon complexation with platinum and palladium. The H-6,6' protons of bpy and dpa in the amino acid complexes are shifted to higher fields, and this could be explained in terms of stronger binding of amino acids than chloride ions to the metal (Sarneski *et al* 1981). The large down-field shifts in the $-CH_3$ groups in these amino acid complexes clearly indicate the sulphur atom coordination to the metal. The 50 Hz $^3J_{Pt-H}$ coupling constants of $^{195}Pt-S-C-H$ fragment in the platinum complexes further supports the sulphur atom complexation (Erickson *et al* 1968). A value of 38 Hz for $^3J_{Pt-H}$ of the $^{195}Pt-N-C-H$

Table 3. ^1H NMR data of $[\text{M}(\text{L-L}) (\text{a-a})]\text{Cl}$ complexes.

Compound	$\delta_{\text{S-CH}_3}^{\text{a}}$	δ_{CH}	$^3J_{\text{Pt-H}}^{\text{b}}$		$\delta_{\text{H}}^{\text{c}}$
			$^{195}\text{Pt-S-C-H}$	$^{195}\text{Pt-N-C-H}$	
$[\text{Pt}(\text{bpy}) (\text{MC})]\text{Cl}$	2.92* (-0.72) ^d	3.98 (0.08)	52	40	8.88, 38 (9.52, 42) ^c
$[\text{Pd}(\text{bpy}) (\text{MC})]\text{Cl}$	2.75 (-0.55)	3.96 (0.10)			8.56 (9.15)
$[\text{Pt}(\text{phen}) (\text{MC})]\text{Cl}$	3.02 (-0.82)	4.04 (0.02)	50	38	9.24, 32 — ^f
$[\text{Pd}(\text{phen}) (\text{MC})]\text{Cl}$	2.98 (-0.78)	4.02 (0.04)			9.02 — ^f
$[\text{Pt}(\text{dpa}) (\text{MC})]\text{Cl}$	2.80 (-0.60)	3.98 (0.08)	50	38	8.40, 28 (8.84, 44)
$[\text{Pd}(\text{dpa}) (\text{MC})]\text{Cl}$	2.74 (-0.54)	4.00 (0.06)			8.20 (8.60)
$[\text{Pt}(\text{phen}) (\text{M})]\text{Cl}$	2.88 (-0.74)	3.80 (0.06)	48	38	9.28, 28 — ^f
$[\text{Pd}(\text{phen}) (\text{M})]\text{Cl}$	2.74 (-0.60)	3.76 (0.1)			9.04 — ^f
$[\text{Pt}(\text{dpa}) (\text{M})]\text{Cl}$	2.60 (-0.46)	3.00 (0.16)	50	38	8.42, 24 (8.84, 44)
$[\text{Pd}(\text{dpa}) (\text{M})]\text{Cl}$	2.56 (-0.42)	3.60 (0.18)			8.22 (8.60)

^a δ -chemical shift (ppm); ^b J coupling constant (Hz); ^c chemical shifts of 6-6' protons of bpy/dpa; ^d chemical shift differences are given in parenthesis relative to the corresponding amino acids. A positive sign denotes upfield shift and a negative sign denotes downfield shift. ^e L-L protons (H-6,6') chemical shifts in $\text{M}(\text{L-L})\text{Cl}_2$ complexes and $^3J_{\text{Pt-H}}$ values. ^f $\text{Pt}(\text{phen})\text{Cl}_2$ and $\text{Pd}(\text{phen})\text{Cl}_2$ data precluded because of solubility. * MC complexes show splitting in CH_3 signals, bpy (6.5 Hz) > dpa (4.5) > phen (2 Hz).

fragment indicates that the nitrogen of the amino group is bonded to platinum and that the complexes have a chair conformation (Erickson *et al* 1968; Sarneski *et al* 1981). This suggests that methyl-cysteine and methionine are bonded to palladium through the amino nitrogen. This is further supported by the presence of a new band in the far-IR region ($550\text{--}555\text{ cm}^{-1}$) assignable to $\nu(\text{M-N})$ vibration (Condrate and Nakamoto 1965). The up-field chemical shifts for $-\text{CH}$ protons in the complexes as against the free amino acids may be interpreted in terms of free $-\text{COO}^-$ group, possibly intermolecularly hydrogen-bonded, to NH proton(s). This is supported by the infrared spectra which show a $15\text{--}20\text{ cm}^{-1}$ higher frequency shift of $\nu(\text{COO}^-)$, as compared to the free amino acids in zwitterion form (Kieft and Nakamoto 1967).

The S-methyl-L-cysteine complexes show the presence of isomers, as detected by ^1H NMR. S-alkyl-cysteine complexes of platinum and palladium show the presence of isomers in solution as well as in the solid state (Theodorou and Hadjiliadis 1985). The spectrum of $[\text{Pt}(\text{bpy})(\text{MC})]\text{Cl}$ shown in figure 1 is typical of the spectra of 1:1 platinum complexes of S-methyl-L-cysteine. The bidentate coordination through sulphur and nitrogen gives ^{195}Pt side bands for all six protons. The presence of two

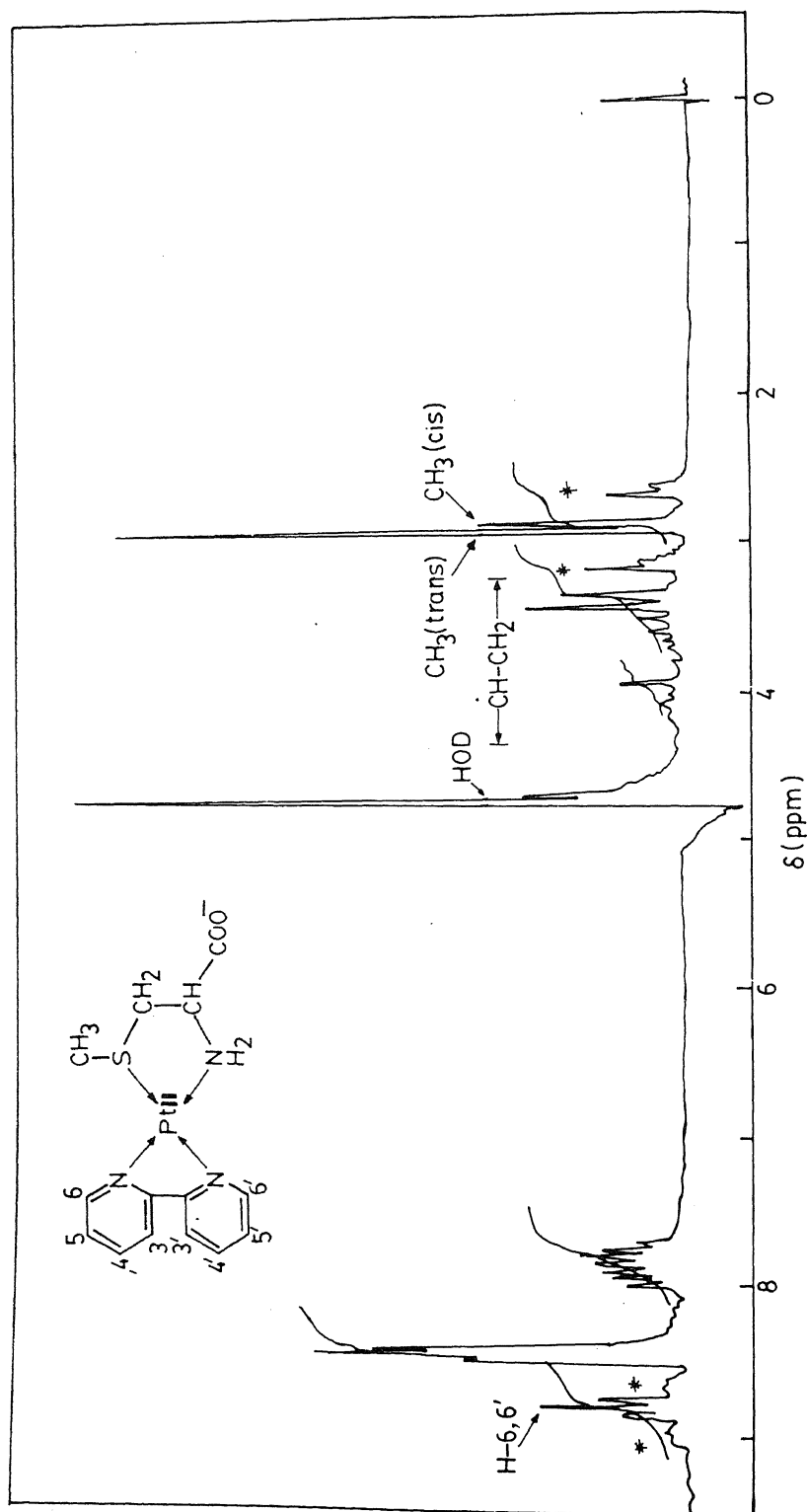


Figure 1. ^1H NMR of $[\text{Pt}(\text{bpy})(\text{MC})]\text{Cl}$ complex in D_2O showing the presence of both *cis* and *trans* isomers. Symmetric ^{195}Pt satellites surrounding the respective signals are indicated by asterisks.

isomers is suggested by the two overlapping 1:4:1 triplets of the methyl signal in 2:1 ratio. The larger peak of this signal can be assigned to the isomer in which CH_3 and COO^- groups are *trans* since their frequencies are less affected by the protonation of the COO^- group (Erickson *et al* 1968).

Recently, $\text{Pt}(\text{bpy})\text{Cl}_2$ has been shown to be anticancer active (Canty and Stevens 1981). The cisplatin shows a nephrotoxic effect which is due to the coordination of protein-bound sulphhydryl groups of the kidney tubule cells to platinum (Borch and Pleasents 1979). These complexes are good models for this cisplatin-protein interaction.

The above complexes are being screened for their anti-cancer activity *in vitro*.

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Potassium ferrocyanide as an analytical reagent for the determination of rhenium

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Abstract. In hydrochloric acid medium, rhenium is reduced to a lower valence using stannous chloride as a reductant. The reduced species of the metal ion forms a stable violet coloured complex with potassium ferrocyanide on heating, which can be quantitatively extracted into isoamyl alcohol and its absorbance measured. The method is free from the interference of anions like sulphate, chloride, oxalate, tartrate and EDTA. Microamounts of U(VI), Cr(VI,III), V(V), Fe(III,II), Cu(II), Co(II), Ni(II), Zn(II) and Pd(II) also do not interfere. The method has a wider Beer's law range of 0-20 $\mu\text{g Re/ml}$ with a Sandell's sensitivity of 0.022 $\mu\text{g/cm}^2$, and is successfully applied to the analysis of different synthetic samples containing micro amounts of rhenium where it compares favourably with the existing methods. The ratio of rhenium : ferrocyanide in the extracted species is found to be 1 : 1 by Job's method of continuous variations and confirmed by the mole ratio method.

Keywords. Potassium ferrocyanide; spectrophotometric determination; rhenium determination.

1. Introduction

A common spectrophotometric method for the determination of rhenium involves extraction of the thiocyanate complex into higher alcohols (Tribalat 1946) and other solvents (Sandell 1959). In the α -furildioxime (Marczenko 1976) method the rhenium complex is measured either in aqueous acetone medium or in a chloroform extract. In the recent past, some new methods (Bag and Chopra 1975; Gangopadhyay *et al* 1976; Majumdar *et al* 1977; Rzhavichev *et al* 1980; Shinde 1984) for determining rhenium have been reported in the literature.

As separation methods may still leave interfering elements in traces, it is advantageous to have determination methods for rhenium which can tolerate the presence of traces of other elements. Keeping this in view, an attempt has been made to develop a simple extractive method for rhenium determination using ferrocyanide as a ligand for the metal ion in the lower valent state in acid medium.

2. Experimental

2.1 Reagents and solutions

A stock solution of rhenium (1 mg/ml) is prepared by dissolving weighed amounts of potassium perrhenate 'Specpure' of Johnson Matthey and Co. in water

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containing a few drops of dilute sulphuric acid. Lower concentrations of the metal ion at the $\mu\text{g/ml}$ level are prepared by suitable dilutions. Potassium ferrocyanide, a 2% solution of the reagent is made by dissolving 2 g of potassium ferrocyanide (BDH, AR) in 100 ml distilled water. It is prepared fresh daily. Stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 20%: 20 g of stannous chloride dihydrate (BDH) are dissolved in 20 ml 1 : 1 HCl by heating till the solution becomes clear. It is then cooled and made up to 100 ml in a volumetric flask with distilled water. Solutions of other elements are prepared by dissolving their suitable salts (CP or AR grade) in distilled water or dilute hydrochloric acid. Isoamyl alcohol (BDH) is distilled and the fraction collected between 128–132°C is used. Hydrochloric acid (BDH) is standardised before use.

2.2 Apparatus

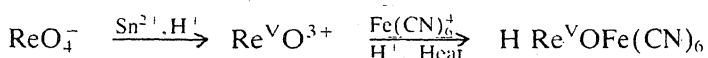
Absorbance measurements are taken on Beckmann DU-2 model ultraviolet spectrophotometer using 1 cm glass cells.

2.3 Procedure

To a sample solution containing $\leq 500 \mu\text{g}$ rhenium are added 6 ml of 10M HCl and 4.5 ml 2% potassium ferrocyanide reagent, followed by 1 ml of 20% stannous chloride. It is gently mixed and made up to 20 ml in a 100 ml beaker. It is heated for 1–1.5 min at 90–95°. The violet coloured species thus formed is cooled and the volume is readjusted to 20 ml with distilled water in a 100 ml separating funnel. The complex is extracted once with an equal volume of isoamyl alcohol for 2 min. The solvent layer is filtered through a Whatman filter No. 41 to remove any suspended droplets of water into a 25 ml volumetric flask. The filter paper is washed twice each time with 1 ml of pure isoamyl alcohol and the flask is filled up to the mark by adding pure solvent. It is gently mixed and the absorbance of the coloured complex is measured at λ_{max} 510 nm against a blank prepared similarly in a 1 cm glass cell using Beckmann DU-2 spectrophotometer.

3. Results and discussion

Stannous chloride is known to reduce Re(VII) to Re(V) contaminated by Re(IV) in simple acid solutions. However, it is probable that the reduction may stop at Re(V) in the presence of suitable complexing ligands. Lower valent rhenium, thus obtained, forms a violet coloured species with ferrocyanide on heating. The chemical reactions involved are assumed to be as follows:



This complex is quantitatively extracted into isoamyl alcohol and the absorbance is measured at λ_{max} 510 nm against a corresponding reagent blank. The absorbance of the complex is influenced by the parameters given in table 1.

Table 1. Dependence of rhenium-ferrocyanide absorbance* on different parameters.

HCl ^a , M	1.0	2.5	2.75	3.0	3.25	3.5	4.0		
Absorbance	0.03	0.095	0.120	0.125	0.125	0.115	0.110		
$K_4Fe(CN)_6 \cdot 3H_2O^b$, ml	0.3	0.5	1.0	2.0	3.0	4.0	4.25	4.5	5.0
2% Absorbance	0.06	0.110	0.125	0.135	0.159	0.170	0.175	0.175	0.175
$SnCl_2 \cdot 2H_2O^c$, ml	0.50	0.75	1.00	1.15	1.25	1.50			
20% Absorbance	0.100	0.125	0.175	0.175	0.170	0.170			
Contact time ^d , min	0.5		1.0		2.0		3.0		
Absorbance	0.150		0.165		0.175		0.175		

*Under initial conditions chosen at random.

Conditions:

(a) Re = 100 μ g, $K_4Fe(CN)_6 \cdot 3H_2O$ (2%) = 1 ml, $SnCl_2 \cdot 2H_2O$ (20%) = 1 ml, heating time = 15 sec, aqueous volume = solvent volume = 20 ml (isoamyl alcohol), equilibration time = 2 min.

(b) HCl = 3M; other conditions are the same as in (a) excepting $K_4Fe(CN)_6 \cdot 3H_2O$.

(c) $K_4Fe(CN)_6 \cdot 3H_2O$ = 4.5 ml; other conditions are the same as in (b) excepting $SnCl_2 \cdot 2H_2O$.

(d) $SnCl_2 \cdot 2H_2O$ = 1 ml; other conditions are the same as in (c) excepting contact time.

3.1 Choice of solvent

Pure chloroform, tribenzylamine in chloroform and isoamyl acetate do not extract the rhenium-ferrocyanide complex at all and the absorbance is found to be nil. Isobutyl methyl ketone and ethyl acetate extract the metal ion only partially, whereas the absorbance is maximum with isoamyl alcohol and hence the choice.

3.2 Effect of acidity

At 1 M HCl, the absorbance of the complex is 0.03 which increases with increase in acid concentration and reaches a maximum of 0.125 in 3.0–3.25 M HCl. Further increase in acidity results in lowering of absorbance.

3.3 Effect of ferrocyanide concentration

The absorbance of the complex is 0.06 if the solution contains 0.3 ml of 2% potassium ferrocyanide. It shows an upward trend if the reagent content is increased. For 4.25–5 ml, the absorbance is optimum at 0.175.

3.4 Effect of stannous chloride as reductant

The absorbance is only 0.10 if the solution contains 0.5 ml of the reductant. It is maximum and maintains constancy at 0.175 for 1–1.15 ml. Beyond 1.15 ml, it shows a gradual decline.

3.5 Equilibration time

Shaking the sample solution containing the metal ion once for 0.5 min with an equal volume of solvent gives an absorbance value of 0.150, which increases to 0.175 for 2–3 min contact time.

3.6 Effect of temperature

At room temperature, the complex formed between reduced rhenium and ferrocyanide is initially yellow in colour which is not found to be stable and slowly changes to violet with time. If the solution is kept undisturbed for 30 min or more, it is converted to a stable violet coloured species. To save time, the solution is heated for 1–1.5 min (i.e. $\sim 95^{\circ}\text{C}$) and complex formation is facilitated. However, heating for a longer time is to be avoided as it results in slight decrease of absorbance.

3.7 Recommended optimum conditions

From the consideration of the above data, it is evident that for $\leq 500\text{ }\mu\text{g}$ of rhenium treating with 3M HCl, 4.5 ml 2% potassium ferrocyanide, 1 ml of 20% stannous chloride in 20 ml aqueous volume, heating for 1–1.5 min at $90\text{--}95^{\circ}$ and equilibrating once with an equal volume of isoamyl for 2 min, transfers the rhenium quantitatively to the solvent phase. The absorbance is measured at λ_{max} 510 nm using a 1 cm glass cell and a Beckmann DU-2 spectrophotometer.

3.8 Stability, reproducibility and observance of Beer's law

The absorbance of the complex is noted after leaving it undisturbed in the cell for different intervals of time. No change in the reading is observed even after over two hours. The reproducibility is tested by performing six different operations with the same amount ($100\text{ }\mu\text{g}$) of the metal ion each time. The absorbance value is found to be the same always confirming that the results are reproducible. Beer's law is obeyed in the range $0\text{--}20\text{ }\mu\text{g}$ Re/ml with a molar extinction coefficient of $8.13 \times 10^3\text{ l.mol}^{-1}\text{ cm}^{-1}$ and Sandell's sensitivity of $0.022\text{ }\mu\text{g/cm}^2$.

3.9 Composition of the complex

The ratio of rhenium to ferrocyanide as 1 : 1 in the extracted species is studied by Job's method of continuous variations (Job 1928) at different wavelengths namely 480 nm, 510 nm, 550 nm and the same is further supported by the mole ratio method (Yoe and Jones 1944). Thus in the present case, an extractable ion association complex $\text{H}[\text{Re}^{\text{V}}\text{OFe}(\text{CN})_6]$ is probably formed.

3.10 Effect of diverse ions

Sulphate (200), chloride (150), oxalate (200), tartrate (100), or EDTA (200) do not influence the absorbance. Acetate (200) and phosphate (200) slightly increase it whereas fluoride (200) slightly decreases it. Figures in parentheses indicate the amount of sodium salts of the anion present in mg.

Pd(II) ($2\text{ }\mu\text{g/ml}$), Cr(VI), V(V), Fe(II, III), Cu(II) ($4\text{ }\mu\text{g/ml}$), Cr(III) ($6\text{ }\mu\text{g/ml}$), Co(II) ($8\text{ }\mu\text{g/ml}$), U(VI), Ni(II) ($20\text{ }\mu\text{g/ml}$), and Zn(II) ($100\text{ }\mu\text{g/ml}$) do not influence the absorbance. Mo(VI), W(VI) and Ru(III) ($4\text{ }\mu\text{g/ml}$) interfere.

3.11 Applications

The method is applicable to the determination of micro amounts of rhenium, especially in those samples which contain trace amounts of other metal ions of great

Table 2. Analysis of synthetic samples by the proposed method.

Sample composition		
Matrix*	Re added μg	Re found μg
Co (200)	100	100
Fe (300)	20	20
V (40)	230	230
Ni (500)	70	70
U (500, 1000)	100	100, 102
Cr (400)	100	99.5
Co (200), Fe (30)	100	99.5
U (500), Fe (100), V (40)	100	100.5
Cr (300), Ni (500)	100	99.0
Cr (100), V (50), Fe (80), Ni (200)	80	81.5

*Figures in parentheses indicate the amount of metal ion in μg .**Table 3.** Comparison of the proposed method with some other methods.

Method	λ_{max}	ϵ ($1 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$)	Reference
Re^{VII} , HCl, thioacetamide, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	400	7.0×10^3	0.0266	Lazarev 1968
Re^{VII} , HCl, thiosalicylic acid, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	410	6.1×10^3	0.03	Tarayan and Gaibakyan 1966
Re^{VII} , HCl, thioglycolic acid, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	320–350	3.6×10^3	0.50	Abramova <i>et al</i> 1968
Re^{VII} , HCl, 2-aminobenzenethiol, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	420	7.5×10^3	0.025	Bag and Chopra 1975
Re^{VII} , strongly acidic, morpholinium morpholine-N-dithiocarbamate	344	4.60×10^3	0.040	Likussar and Beyer 1973
Re^{VII} , HCl, N-(2-pyridyl) α -thio picotinamide, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	—	7.20×10^3	0.026	Bag and Ramesh 1976
Proposed method	510	8.13×10^3	0.022	—

analytical importance and which seriously interfere in the determination of the former. The results of analysis are quite in agreement with the amount of the metal ion initially added to the sample (table 2). The method is simple, cheap, rapid and makes use of commonly available reagents. It compares favourably with the existing methods often employed for the microdetermination of rhenium (table 3).

4. Conclusion

A selective and sensitive method for the determination of trace amounts of rhenium is developed by extraction of rhenium-ferrocyanide complex into iso-amyl alcohol using a reductant in acid medium. It has a Beer's law range of 0–20 μg Re/ml with a molar extinction coefficient of $8.310 \times 10^3 \text{ l. mol}^{-1} \text{ cm}^{-1}$ and

Sandell's sensitivity of $0.022 \mu\text{g}/\text{cm}^2$. The complex is stable for more than two hours and the results obtained are reproducible. The method tolerates the interference of several analytically important elements. The validity of the method is tested by satisfactory analysis of several synthetic samples.

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Kinetics and mechanism of anation of hydroxopentaaquo chromium(III) ion by L-histidine in water ethanol mixtures of different dielectric constant

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Abstract. The kinetics of substitution of aquo ligands from hydroxopentaaquo chromium(III) ion by L-histidine in water ethanol medium has been studied spectrophotometrically. The rate law involving the ion pair formation has been established. The activation parameters have been calculated and compared with other substitution reactions. Variation of dielectric constant of the medium was used as a tool for the mechanistic conclusion. Considering all the results, a mechanism involving the prior formation of ion pair followed by associative interchange (I_a) has been suggested.

Keywords. Anation; hydroxopentaaquo chromium(III) ion; amino acid; ion pair; dielectric variation; associative interchange.

1. Introduction

Anation reactions of hexaaquo chromium(III) ion have been studied by different authors (Banerjea and Dutta Chaudhury 1968; Banerjea and Chatterjee 1969; Banerjea and Sarkar 1972; Hartley 1968; Bhattacharya and De 1983; Mandal and De 1980) and it is a very interesting fact that both I_d and I_a mechanisms have been proposed. Kinetic study with hydroxopentaaquo chromium(III) ion has been a subject of recent interest (Niogy and De 1983, 1984, 1985). Hydroxopentaaquo chromium(III) complex is distinctly different from the hexaaquo complex due to the presence of the hydroxo group in the former species. Thus expecting some interesting results we planned to study the substitution kinetics of the aquo ligands from the title complex by different polydentate ligands in water ethanol medium. The present paper deals with the findings of the reaction between the title complex and L-histidine in water ethanol mixtures of different dielectric constants.

2. Materials and methods

The reactant $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ having absorption maxima at 410 nm ($\log \epsilon$, 1.52) and 570 nm ($\log \epsilon$, 1.21) was prepared by the method of Moor and Basolo (1965). The solution of $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}]$ (complex 1) was obtained *in situ* from the hexaaquo species by adjusting the pH to 5.0. The pK_a of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ being 3.8 a

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solution of this at pH 5 with absorption maxima at 430 nm ($\log \epsilon$, 1.447) and 590 nm ($\log \epsilon$, 1.255), represents complex 1. The product of reaction between $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})](\text{ClO}_4)_2$ and L-histidine was prepared by mixing these ion different molar ratios of 1:1, 1:2 and 1:3 thermostated at 50°C for 48 hours. The absorption spectra of the resultant maroon coloured solutions were taken and found that solutions with 1:2 and 1:3 compositions exhibited identical natures having maximum absorption at 510 nm ($\log \epsilon$, 1.68). The composition of the product in the reaction mixture was checked by Job methods of continuous variation and found to have 1:2 metal ligand ratio in the product (figure 1). The maroon coloured solid isolated from the reaction between (complex-I) and L-histidine was analysed for $[\text{Cr}(\text{Hist})_2](\text{ClO}_4)_4$. A similar cobalt(III) complex $[\text{Co}(\text{Hist})_2]^+$ was isolated by Zompa (1969) for structural study.

3. Kinetic run

All the kinetic runs were followed by measuring absorbances at 510 nm (using a Hilger UVISPEK Spectrophotometer) where a substantial difference existed in the spectra of complex I and complex II and the condition of the applicability of the first-order rate law was maintained throughout. The pseudo first-order rate constants (k_{obs}) were obtained by plotting $\log(D_\infty - D_0)/(D_\infty - D_t)$ versus time

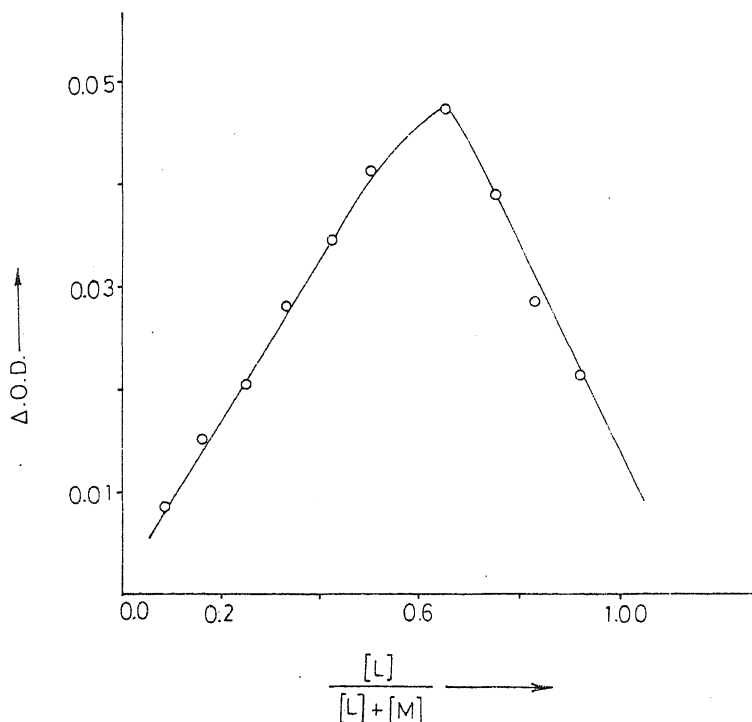


Figure 1. Jobs plot of $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ histidine complex at pH 5.0, $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+} = [\text{Hist.H}] = 0.005 \text{ M}$.

where D_{∞} , D_t and D_0 are the optical density values at infinite time, at the end of time t and at the beginning of the reaction respectively.

4. Results and discussion

4.1 Effect of varying [complex I] on the rate constant

Three sets of experiments were carried out at 35°C maintaining a constant [ligand] of 0.05 M, ionic strength 0.08 M, pH 5 and varying [complex I] from 0.0025 to 0.004 M. The values of pseudo first-order rate constant k_{obs} ($\times 10^4$) were found to be 3.20, 3.15 and 3.11 sec^{-1} at [complex I] 0.0025 M, 0.0035 M and 0.004 M respectively. Thus the reaction rate is first order with respect to [complex I] i.e.

$$d[\text{complex II}]/dt = k_{\text{obs}}[\text{complex I}]$$

4.2 Effect of varying pH on rate constant

At fixed [complex I] (0.0025 M), [ligand] (0.025 M), ionic strength μ (0.08 M) the values of pseudo first-order rate constant ($k_{\text{obs}} \times 10^5 \text{ sec}^{-1}$) at 35°C are shown in figure 2. The pH of the medium was adjusted by adding NaOH or HClO₄. To

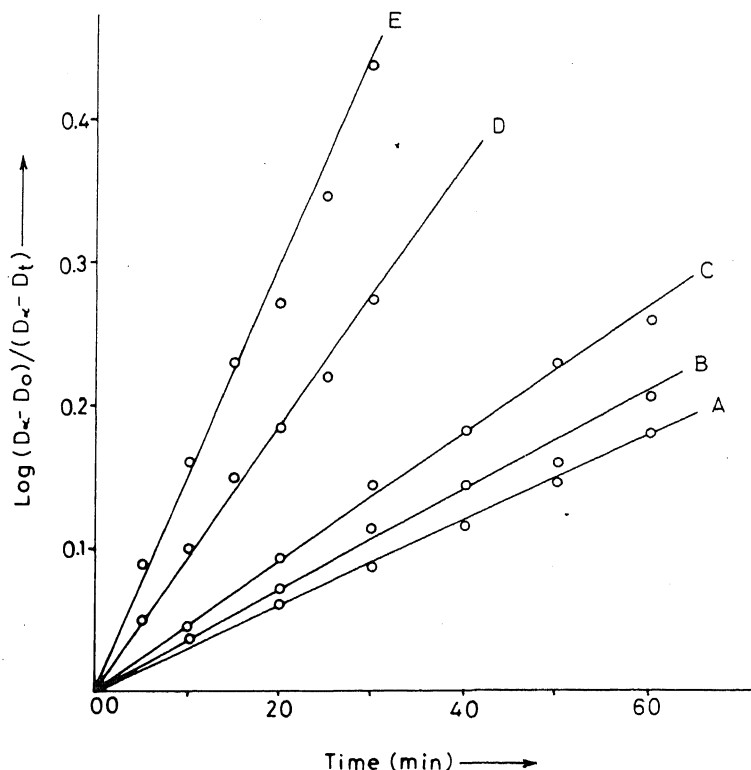
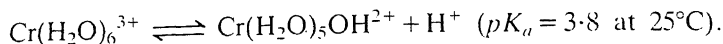


Figure 2. Plot of $\log (D_{\infty} - D_0) / (D_{\infty} - D_t)$ vs. time at 35°C. [complex I] = 0.0025 M, [Hist.H] = 0.025 M. pH = A) 4.54, B) 4.8, C) 5.0, D) 5.32 and E) 5.51.

explain the above results, the following equilibrium is considered necessary (Basolo and Pearson 1977).

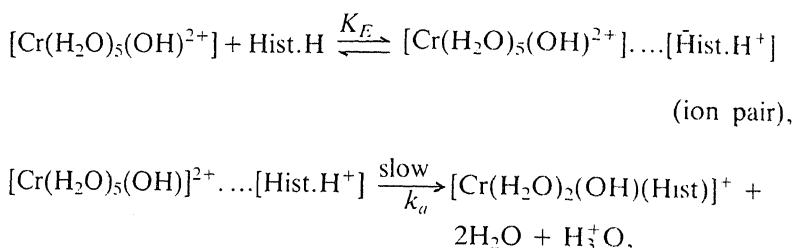


As the pH of the medium is decreased the ratio of [hydroxopentaaquo chromium(III)] : [hexaaquo chromium(III)] is also decreased thereby decreasing the reaction rate. Enhanced reactivity of hydroxopentaaquo complex is due to the well-known labilising effect of the hydroxide ion adjacent to the water ligand by virtue of its lone pair of electrons, capable of exerting a strong electromeric effect. The pK values of L-histidine are $pK_1 = 2.28$, $pK_2 = 6.97$ and $pK_3 = 9.63$; so at the above mentioned pH range the ligand remains mainly in the zwitterionic form. Further increase of pH changes the zwitterionic form of histidine into the anionic form which may increase the rate.

4.3 Effect of varying [ligand] on rate constant

Maintaining a constant [complex I] (0.0025 M) ionic strength 0.08 M, pH 5, the concentration of the ligand was varied in the range of 0.0187 to 0.075 M. k_{obs} values were found to increase with ligand concentration but gradually reached a limiting rate as shown in figure 3a. The results suggest ion pair formation prior to the rate determining step.

The following scheme can be proposed to explain the nature of variation of incoming [ligand] on reaction rate



where k_a is the anation rate constant and K_E is the ion pair equilibrium constant. From the above reaction scheme the following rate law has been established

$$\begin{aligned} \frac{d[\text{complex II}]}{dt} &= \frac{k_a K_E [\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}]_{\text{total}} [\text{Hist.H}]}{1 + K_E [\text{Hist.H}]} \\ &= k_{\text{obs}} [\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}]_{\text{total}}, \end{aligned} \quad (1)$$

where $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}]_{\text{total}}$ = concentration of total amount of unreacted complex I in solution.

$$\text{Therefore } k_{\text{obs}} = \frac{k_a K_E [\text{Hist.H}]}{1 + K_E [\text{Hist.H}]}, \text{ and} \quad (2)$$

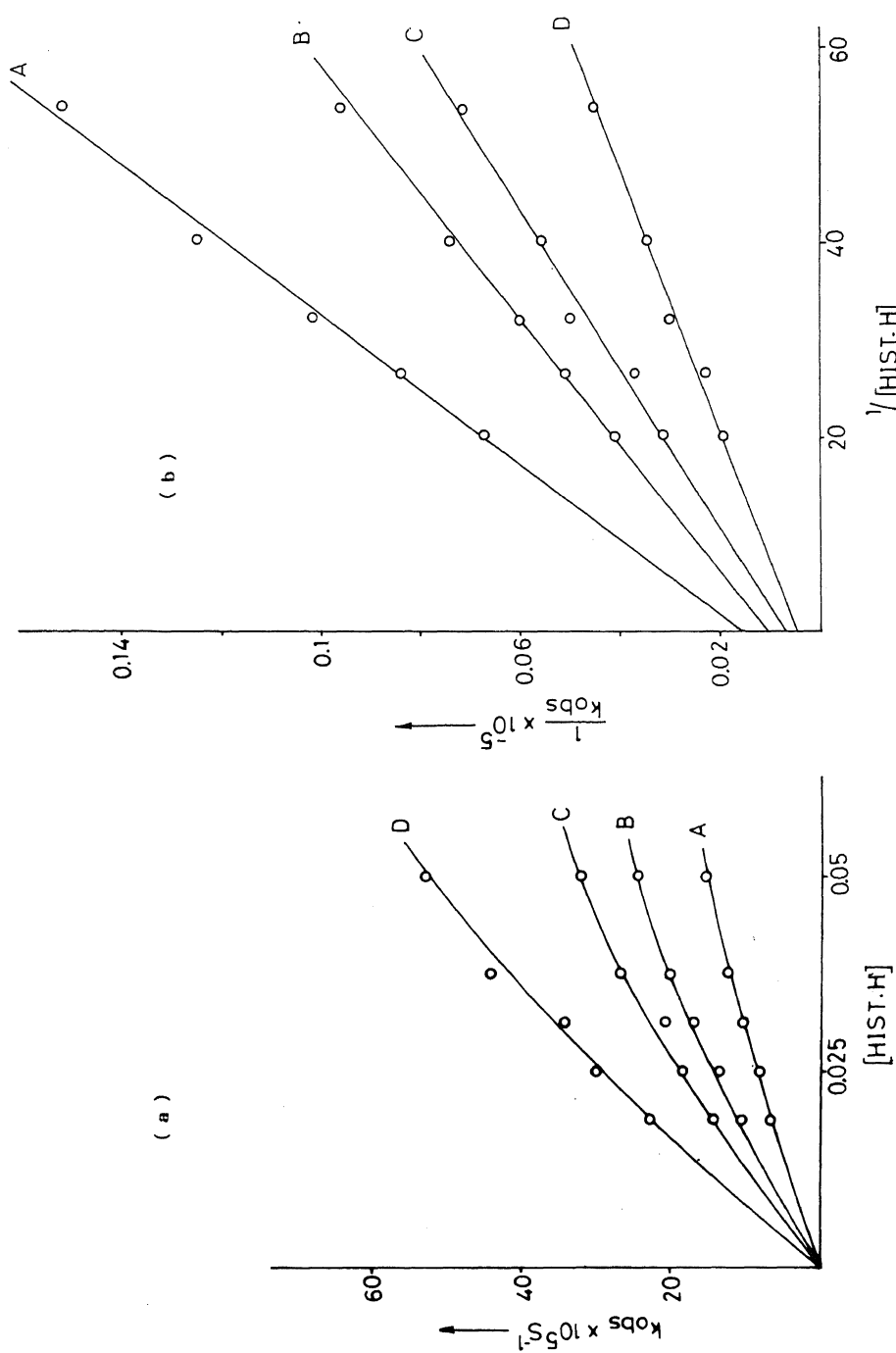


Figure 3 a. Variation of k_{obs} with $[\text{Hist.H}]$ at different temperatures, $[\text{complex I}] = 0.0025 \text{ M}$, $\text{pH} = 5.0$. A) 25°C, B) 30°C, C) 35°C, D) 40°C. b. Plot of $1/k_{\text{obs}}$ vs. $1/[\text{Hist.H}]$ at different temperatures.

$$1/k_{\text{obs}} = 1/k_a + 1/k_a K_E [\text{Hist.H}]. \quad (3)$$

So the plot of $1/k_{\text{obs}}$ vs $1/[\text{Hist.H}]$ should be linear with intercept $1/k_a$ and slope $1/k_a K_E$. This is found to be so (figure 3b). Graphically determined k_a and K_E values are presented in table 1. Results of anation of some analogous systems are cited in table 2 for comparison. It appears from the table that there is definite dependence of the rate of reaction on the nature of the incoming ligand. The anation rate of the title complex is high in comparison with the isotopic water exchange process (Thusius 1971), which suggests an associative interchange mechanism in the substitution reaction.

4.4 Effect of ionic strength on reaction rate

Maintaining a constant [complex I] (0.0025 M) [ligand] (0.025 M) and pH 5, the ionic strength of the reaction mixture was changed by the addition of sodium

Table 1. Comparison of k_a , K_E and activation parameters of analogous systems.

System	$k_a \times 10^5 (\text{s}^{-1})$	K_E ($\text{dm}^3 \text{mol}^{-1}$)	$\Delta H^\ddagger$ kJmol $^{-1}$	$\Delta S^\ddagger$ Jkmol $^{-1}$	Reference
Cr(H ₂ O) ₆ ³⁺ - OH ₂ (ex)	0.41 ^a	—	109.2	(+11.7)	Hunt and Plane (1954)
Cr(H ₂ O) ₅ (OH) ²⁺ - OH ₂ (ex)	<10.0 ^a	—	—	—	Thusius (1971)
Cr(H ₂ O) ₅ (OH) ²⁺ + DL-alanine	39.9 ^b	4.35	33.7	(-199.6)	Niogy and De (1983)
Cr(H ₂ O) ₅ (OH) ²⁺ + DL-phenylalanine	32.32 ^b	31.4	53.4	(-134.5)	Niogy and De (1984)
Cr(H ₂ O) ₅ (OH) ²⁺ + β -alanine	83.00 ^b	12.77	48.8	(-144.0)	Niogy and De (1984)
Cr(H ₂ O) ₅ (OH) ²⁺ + aspartic acid	73.7 ^b	80.00	45.4	(-156.5)	Niogy and De (1985)
Cr(H ₂ O) ₅ (OH) ²⁺ + L-histidine	140.0 ^b	6.8	53.06	(-113.7)	Present work

^a At 25°C; ^b at 35°C.

Table 2. Values of interchange rate constant (k_a), and the activation parameters for anation by L-histidine at different temperatures and in different solvent media.

Temperature (° K)	30% (v/v) ethanol/water		20% (v/v) EtOH/water		10% (v/v) EtOH/water	
	$k_a \times 10^4 \text{S}^{-1}$	K_E	$k_a \times 10^4 \text{S}^{-1}$	K_E	$k_a \times 10^4 \text{S}^{-1}$	K_E
298	6.66	5.77	—	—	—	—
303	9.71	6.31	8.4	6.1	6.62	5.9
308	14.00	6.8	11.01	6.5	9.08	6.11
313	19.55	7.2	18.00	6.95	16.20	6.80
$\Delta H^\ddagger$	13.31 kcal/mol		14.18 kcal/mol		16.01 kcal/mol	
$\Delta S^\ddagger$	-28.50 e.u.		-25.80 e.u.		-20.15 e.u.	

perchlorate. It was observed that at 35°C the pseudo first-order rate constants were 16.6×10^{-5} , 16.3×10^{-5} and 15.8×10^{-5} , at ionic strengths 0.08, 0.2 and 0.3 M respectively. Considering the net charge of zwitterionic histidine to be zero, the results follow the simple Debye-Huckel theory.

By changing the ionic strength of the medium with sodium nitrate the $k_{\text{obs}} (\times 10^5)$ values were found to be 30.7, 43.7 and 48.3 sec^{-1} at ionic strength 0.1, 0.2 and 0.3 M, respectively. This increase in rate is due to the labilising effect arising out of the specific attack of the nitrate ions on the coordinated water molecules. This typical type of ionic strength effect was also observed by different authors (Brown and Harris 1968; Van Eldik 1980).

4.5 Effect of temperature on reaction rate

The temperature effect was studied at four different temperatures for different ligand concentrations in 30% ethanol. The values for anation rate constants (k_a) are calculated and presented in table 2. Activation parameters are calculated using the Eyring plot of $\log k_a$ versus $1/T$ and checked by the least squares method.

A lower $\Delta H^\ddagger$ (13.3 kcal/mol) and a negative $\Delta S^\ddagger$ (-28.51 e.u) suggests a definite ligand participation in the transition state.

4.6 Effect of varying dielectric constant on the rate of reaction

The influence of solvent dielectric constant on rate was studied at three different temperatures in three different ethanol water mixtures. In each set ligand concentration was varied from 0.019 M to 0.075 M at a fixed [complex I] (0.0025 M), pH 5.0 and ionic strength 0.08 M. It has been observed that the pseudo first-order rate constants increase with the decrease of dielectric constant of the medium. As the pseudo first-order rate constant k_{obs} consists of K_E (outersphere association constant) and k_a (interchange rate constant), the evaluation of both K_E and k_a is necessary in different dielectric constant. The k_a and K_E values are determined graphically as usual and the results are given in table 2. It appears from the table that both k_a and K_E values are increased with the decrease of the dielectric constant of the medium. Plot of $\log k_a$ versus $1/D$ were drawn using the Laidler and Eyring equation for the effect of dielectric constant of solvent on rates of reaction between an ionic and a zwitterionic species

$$\frac{d \ln k_a}{d(1/D)} = \frac{e^2 Z^2}{2kT} (1/r_1 - 1/r^*) , \quad (4)$$

where D is the dielectric constant of the medium, Ze is the ionic charge, r_1 is the effective radius of the ion pair, r^* is the radius of the activated species. The plots are linear with positive slope and the magnitude of the slope decreases with increase in temperature as shown in figure 4.

Activation parameters are also calculated from the linear Eyring plot for the reaction in 20% and 10% ethanol medium. Results are given in table 2.

5. Mechanism and conclusion

The reaction between $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ and histidine (in zwitterionic form) involves outersphere association between the two reacting species followed by an

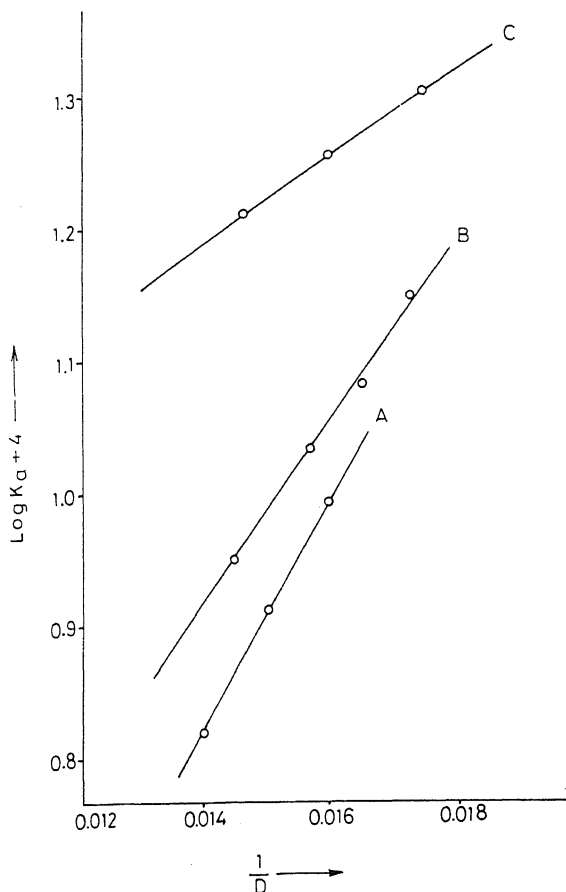


Figure 4. Plot of $\log k_a$ vs. $1/D$ at A) 30°C, B) 35°C, C) 40°C.

associative interchange process where both bond-breaking and bond-making are equally important. The ligand OH^- , being a strong π donor, facilitates the loss of water ligand in the *trans* position. The activated complex formation through outersphere association is stabilized by hydrogen bonding. In this activated complex the carboxylate ion of histidine is able to form a weak bond (figure 5). The above assumption are supported by the rate data. The rate of anation by histidine is faster than that of isotopic water exchange (Thusius 1971). The lower $\Delta H^\ddagger$ and negative $\Delta S^\ddagger$ suggest significant associative character of the interchange process. In the associative interchange process the rupture of the Cr(III)-OH_2 bond already present and the formation of the new Cr(III)-L bond are equally important in the activated state, for this reason the positive enthalpy change due to rupture of Cr(III)-OH_2 bond is partially compensated by the negative enthalpy change due to bond formation by the incoming ligand. Thus a lower $\Delta H^\ddagger$ is noticed. The above conclusion is supported by the results obtained in the variation of dielectric constant. The increase in K_F with the decrease of dielectric constant is quite logical because a medium of low dielectric constant favours ion pair formation. In case of

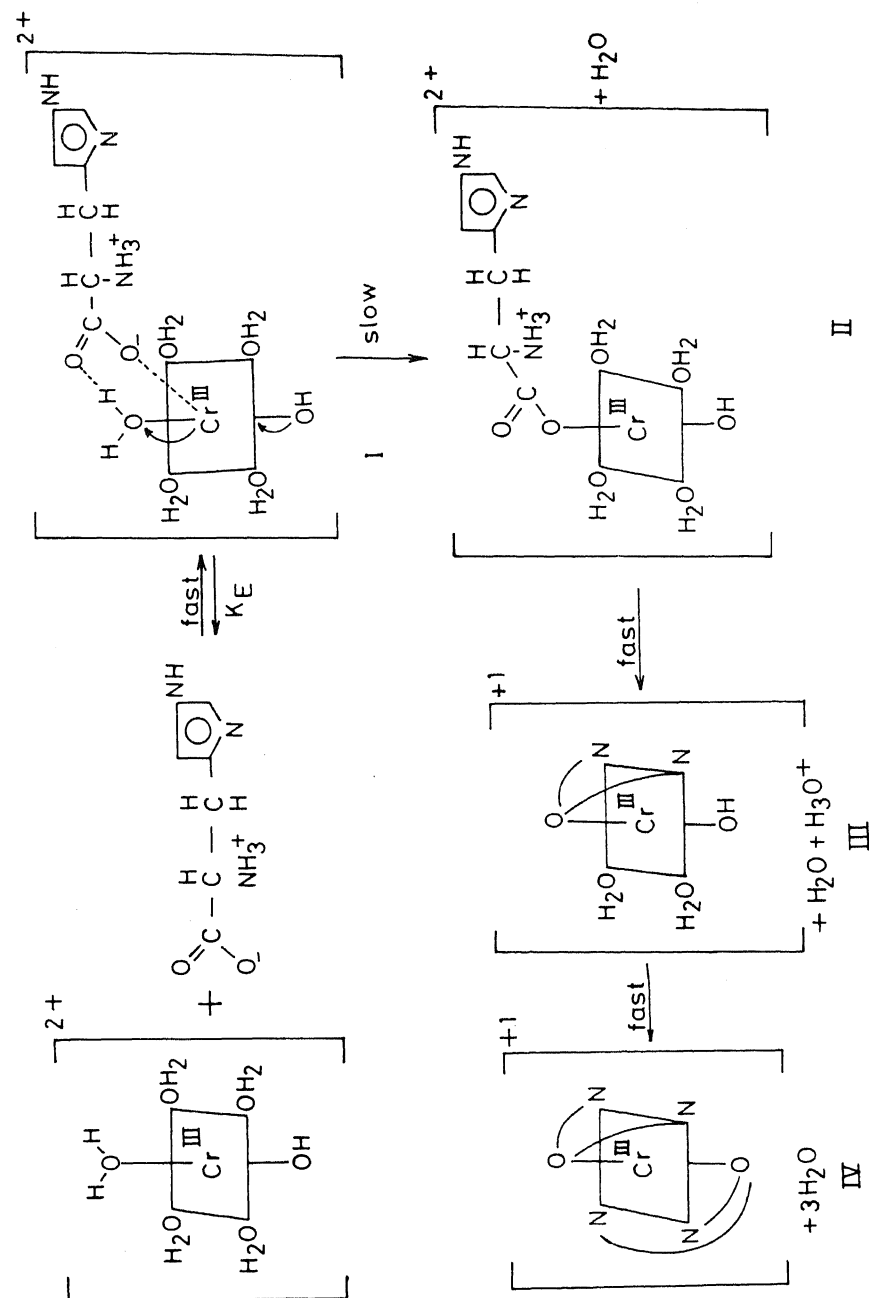


Figure 5. Probable mechanism for the anation process.

associative activation generally, r^* (radius of activated species) is greater than that of r_1 (effective radius of the ion pair).

So the plot of $\log k_a$ versus $1/D$ (following the Laider Eyring equation 4) should be a straight line with positive slope and the magnitude of the slope should decrease with the increase in temperature (Panasyuk and Reiter 1966). This has actually been observed in our study as shown in figure 4. Similar solvent dependence on the reaction rate of base hydrolysis of iso-thiocyanato pentamine complexes of cobalt(III), chromium(III) and rhodium(III) in aqueous organic mixed solvent is also found in the literature (Banerjea *et al* 1983).

The small increase in $\Delta H^\ddagger$ with the increase in dielectric constant of the medium is also supported by the fact that a medium with higher dielectric constant diminishes the possibility of interaction between the cationic complex I and the negative end of the zwitterionic histidine, and automatically needs some higher energy of activation.

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Synthesis and characterization of adducts of stannous chloride with Schiff bases

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Abstract. Some new adducts of tin(II) have been synthesized by the reaction of anhydrous stannous chloride with monofunctional bidentate and bifunctional tetradentate Schiff bases in an oxygen-free nitrogen atmosphere using tetrahydrofuran as the reaction medium. An attempt has been made to probe their structures by elemental analyses, molecular weight determination, conductivity measurement, and IR, ^1H NMR and Mössbauer spectral studies.

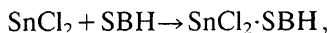
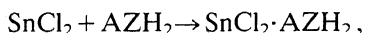
Keywords. Anhydrous stannous chloride; Schiff bases; PMR spectra; IR spectra; Mössbauer spectra.

1. Introduction

Despite the phenomenal growth in coordination chemistry of inorganic and organometallic tin(IV) derivatives, only a limited amount of work has been carried out on the tin(II) Schiff base complexes (Hobday and Smith 1971; Stocco *et al* 1974; Ewings *et al* 1976; Varshney and Tandon 1984, 1985; Varshney *et al* 1986). In view of this, it was considered of interest to synthesize and characterize the tin(II) complexes with monofunctional bidentate and bifunctional tetradentate Schiff bases. The results of these investigations are reported in this paper.

2. Discussion

The reactions of anhydrous stannous chloride with azine and Schiff base containing fluorine in 1:1 molar ratios in tetrahydrofuran may be represented by the following equation:



where $\text{AZH}_2 \rightarrow$ azines

$\text{SBH} \rightarrow$ Schiff base containing fluorine.

These reactions are quite facile and the colour of the reaction mixture changes from light yellow to dark yellow and red. These complexes (table 1) are soluble in

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Table I. Synthesis and characteristics of tin(II) adducts.

Tin compound (g)	Ligand (g)	Molar ratio	Yield %	Product and characteristics (colour state)	M.P. (°C)	Analysis %			Mol. wt. Found (Calcd)
						Sn Found (Calcd)	N Found (Calcd)	Cl Found (Calcd)	
SnCl ₂ 0.527	C ₆ H ₅ OHCH:NN:CHHOH ₄ C ₆ C ₁₄ H ₁₂ N ₂ O ₂ 0.667	1:1	80	SnCl ₂ ·C ₁₄ H ₁₂ N ₂ O ₂ Yellow solid	235	26.96 (27.62)	6.12 (6.52)	16.03 (16.52)	402.3 (429.7)
SnCl ₂ 0.627	C ₁₀ H ₆ OHCH:NN:HCHOC ₆ H ₁₀ C ₂₂ H ₁₆ N ₂ O ₂ 1.124	1:1	82	SnCl ₂ ·C ₂₂ H ₁₆ N ₂ O ₂ Yellow solid	260	21.93 (22.41)	5.07 (5.28)	12.94 (13.40)	507.2 (529.7)
SnCl ₂ 0.870	C ₆ H ₅ OHCH ₃ C:NN:CCH ₃ OHHC ₆ C ₁₆ H ₁₆ N ₂ O ₂ 1.229	1:1	83	SnCl ₂ ·C ₁₆ N ₂ O ₂ Yellow solid	230	25.16 (25.93)	5.82 (6.18)	15.04 (15.51)	438.3 (457.7)
SnCl ₂ 0.235	HOC ₁₀ H ₆ CH:NC ₆ H ₄ F-p C ₁₇ H ₁₂ NFO 0.328	1:1	85	SnCl ₂ ·C ₁₇ H ₁₂ NFO Yellow solid	175	25.93 (26.11)	2.93 (3.08)	14.92 (15.61)	445.4 (454.7)
SnCl ₂ 0.623	HOC ₆ H ₄ CH:NC ₆ H ₄ F-p C ₁₃ H ₁₀ NFO 0.673	1:1	83	SnCl ₂ ·C ₁₃ H ₁₀ NFO Light yellow solid	187	28.85 (29.33)	3.01 (3.46)	17.04 (17.54)	386.4 (404.7)
SnCl ₂ 0.427	HOC ₆ H ₄ CCH ₃ :NC ₆ H ₄ F-p C ₁₄ H ₁₂ NFO 0.515	1:1	82	SnCl ₂ ·C ₁₄ H ₁₂ NFO Light yellow solid	145	27.83 (28.34)	3.02 (3.34)	16.23 (16.96)	403.5 (418.7)

DMSO, DMF, methanol and chloroform but are insoluble in benzene. The molar conductance of 10^{-3} M solutions of the adducts in DMF lies in the range $10\text{--}18\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$, indicating their non-electrolytic behaviour. Molecular weight determinations indicate their monomeric nature.

2.1 IR spectra

In the IR spectra of the ligands, a strong broad band due to νOH appears in the region, $3050\text{--}2650\text{ cm}^{-1}$ indicating the presence of hydrogen-bonding. However, in the spectra of the adducts, two bands appear in the region, $3500\text{--}2700\text{ cm}^{-1}$ and which may be assigned to the stretching vibrations of the OH group. The presence of two bands in this region, indicates that only one of the two OH groups coordinates with the metal atom, while the other one probably remains hydrogen-bonded to the nitrogen. This band overlaps with the C-H stretching vibration in this region.

A strong band due to $\nu(\text{C}=\text{N})$ is observed in the ligands at $\sim 1625\text{ cm}^{-1}$, and in the complexes this splits into two as only one of the two azomethine nitrogens can coordinate with the metal ion due to steric hindrance. The shift of one of the two bands to lower frequencies may be due to the metal-ligand π -electron interaction involving one of the azomethine nitrogens. The new bands observed in the spectra of tin complexes in the regions, $540\text{--}560\text{ cm}^{-1}$, 430 cm^{-1} and around 325 cm^{-1} may be assigned to $\text{Sn}\leftarrow\text{N}$, $\text{Sn}\leftarrow\text{O}$ and $\text{Sn}\text{--Cl}$ stretching modes of vibration.

2.2 PMR spectra

The mode of coordination discussed above gets further support from the PMR spectra of the ligand and its 1:1 tin complexes. A broad singlet at $\delta 12.50$ in the spectra of ligand, assignable to the hydrogen-bonded OH, shifts to the lower range in tin complexes. This indicates the co-ordination of the metal atom through the oxygen of the ligand moiety.

The one proton singlet in ligand at $\delta 8.80$ ppm assignable to the azomethine proton is shifted downfield in the complexes and appears at $\delta 9.10$ ppm. This is probably due to the donation of a lone pair of electrons by the nitrogen to the central metal atom to form a coordinate linkage.

2.3 Mössbauer spectra

The Mössbauer isomer shift values of adducts of tin(II) chloride were found in the range ($3.72\text{--}3.82\text{ mms}^{-1}$) prescribed for +2 oxidation state of tin ($+2.5$ to 4.5 mms^{-1}) and are much lower than the values of δ for SnCl_2 (4.12 mm sec^{-1}) indicating the interaction of the nitrogen of the $>\text{C}=\text{N}$ group with the metal atom (Parish 1972; Huggins *et al* 1969). The quadrupole splitting data ($1.82\text{--}2.52\text{ mm sec}^{-1}$) shows that the charge distribution around the tin atom is not spherical.

On the basis of the above evidence, the following tentative structure with salicylaldehydeazine as ligand can be assigned to these newly synthesized derivatives.

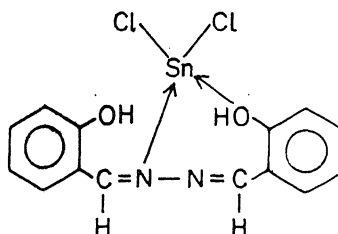


Chart 1.

3. Experimental

All the reactions were carried out under anhydrous conditions in an oxygen-free nitrogen atmosphere.

3.1 Materials

Stannous chloride was dehydrated by dissolving in acetic anhydride (Gell and Zeldin 1975) ligand were prepared as reported earlier (Singh *et al* 1980; Mookerjee *et al* 1983).

3.2 Analytical methods and physical measurements

The complexes were analysed by the literature method (Varshney and Tandon 1985) and the molecular weights were determined by the Rast method. Molar conductance measurements were made in anhydrous dimethyl formamide at $36 \pm 1^\circ\text{C}$ using a Systronics Conductivity Bridge, Model-305. The details of spectroscopic measurements are similar to those reported earlier (Varshney *et al* 1986).

3.3 Synthesis of tin(II) Schiff base adducts

To a weighed amount of tin (II) chloride (1 mole) was added a calculated amount of ligand (1 mole) with dry tetrahydrofuran as the reaction medium in a nitrogen atmosphere. The reaction started instantaneously, followed by colour change. To ensure completion of the reaction, the contents were stirred, using a magnetic stirrer, for three to four hours. The excess of solvent was removed and the compound dried in vacuo, after repeated washing with cyclohexane and benzene.

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Ligand based redox series. Comments on its pattern and search for a parallel proton transfer series

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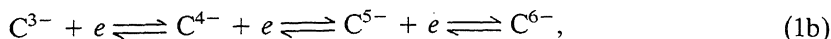
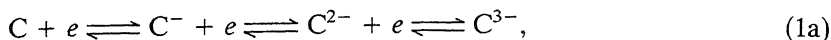
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Abstract. Ligand based redox series in *tris*-bipyridyl complexes of d^6 metal ions and *tris*-*o*-semiquinone complex of Cr(III) follow a general pattern. It is demonstrated that it is possible to look for an isothermodynamic proton transfer series. In the present study orthophosphoric acid is singled out. Implications of such correlations are discussed.

Keywords. Redox series; proton transfer series; isothermodynamic; *tris*-bipyridyl complexes; orthophosphoric acid.

Ligands having unsaturation (e.g., azo, α -azoimine, α -diimine etc. functions) are generally found to be electrochemically active. Consequently the metal complexes of such ligands often display electron transfer reactions which are characteristic of the coordinated ligand fragments. The molecular orbitals involved in these processes have negligible contribution from the metal ion. On the availability of such ligand-centred orbitals depends the number of electrons that can be transferred. In electrochemical experiments the characteristic potentials appear, in most cases, at some intervals forming a redox series. Recently Vlcek (1982) has critically reviewed various aspects – theoretical and thermodynamic – of different ligand based redox series with special attention to those obtained in *tris*-bipyridyl (bpy) complexes. So far *tris*-bpy and *tris*-*o*-semiquinone systems have been found most suitable for studying such phenomenon. Herein we try to recognise that the redox series observed in cases where the natural termination of the series occurs follow a simple general pattern. [By natural termination we mean, ligand dissociation is not associated with any stage of reduction. For example, in case of $\text{Rh}(\text{bpy})_3^{3+}$, first reduction is followed by fast elimination of a bpy ligand (Kew *et al* 1974).] In doing so we also realise that it is possible to construct an isothermodynamic proton transfer series.

Tris-bpy complexes of d^6 metal ions have been studied most extensively by electrochemical techniques in connection with the phenomenon under discussion. The available potential data (Tokel-Takvoryan *et al* 1973; Weiner and Basu 1980; Elliott 1980; Elliott *et al* 1985; Kahl *et al* 1978) for these complexes reveal that a maximum of six electrons can be transferred on to the ligand moieties (the presence of three bpy units sets this limit) in two distinct sets – each set comprising three electrons. The redox series observed in these systems can be schematically represented by (1a) and (1b) where C is a complex species capable of undergoing ligand reductions. An analogous series involving proton transfer will be as shown in (2) where AH_3^{3+} is a tribasic acid.



We want to establish a one-to-one correspondence between the two series, (1) and (2), from the thermodynamic point of view. To do so a relation is sought between the pK values of the acid and the redox potentials in (1a) or (1b). The pK values of orthophosphoric acid, chosen as a model of AH_3^+ , are plotted against the two sets of the redox potentials in various *tris*-bpy complexes of d^6 metal ions (figure 1). The plots are found to be essentially linear. Evidently these suggest that the thermodynamics of the exchange of the two types of particles in the chosen systems are similar. To understand the meaning of the present correlation, we consider the thermodynamics of proton transfer of orthophosphoric acid in some details.

A unique property of H_3PO_4 , an oxy acid, is that its K values maintain the ratio $1:10^{-5}:10^{-10}$ (Pauling 1967). In the undissociated form all the three protons have an identical electronic environment. This property, as indicated by the ratio, is not lost in the subsequent dissociations. The difference in the corresponding free energy values is controlled largely by the two factors— ΔG_e , an electronic one which governs the gas phase vertical proton affinity, and ΔG_s , the solvation of the

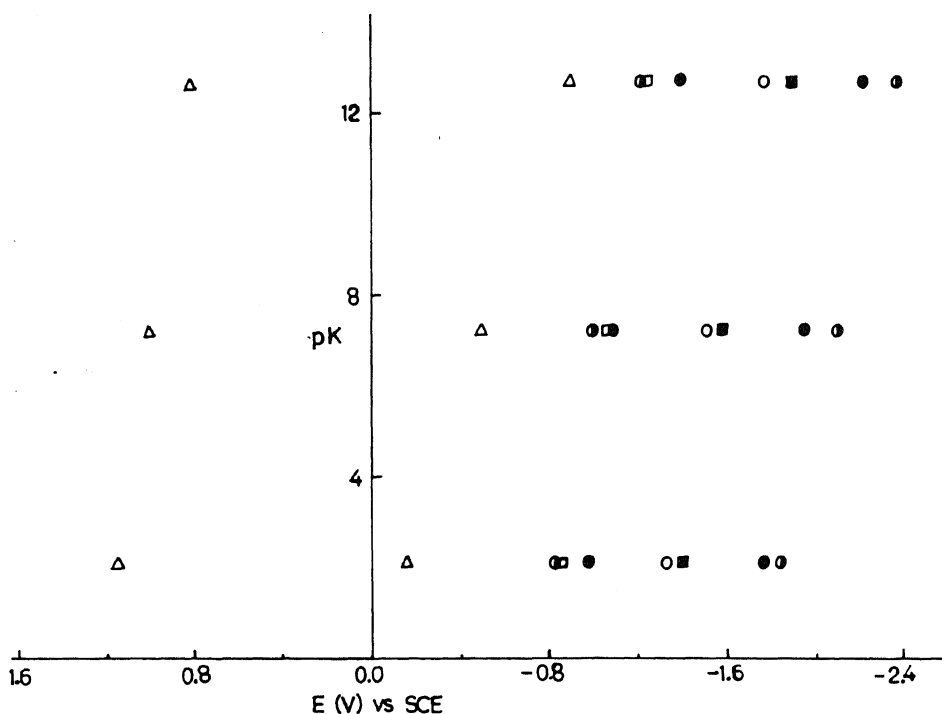


Figure 1. Relation between the pK values of H_3PO_4 and the potentials of the ligand based redox processes in $Ru(bpy)_3^{2+}$ [○], $Ru(\text{substituted } bpy)_3^{2+}$ [●], $Fe(P^+bpy)_3$ [□], $Fe(bpy)_3^{2+}$ [■], $Ir(bpy)_3^{3+}$ [○], and $Cr(o\text{-semiquinone})_3$ [Δ].

various ions generated during dissociations. Since the pK values are more or less equispaced, it follows that $\Delta G_e(1) \propto \Delta G_e(2) \propto \Delta G_e(3)$, and $\Delta G_s(1) \propto \Delta G_s(2) \propto \Delta G_s(3)$, while the numerals indicate the level of dissociation. It is implicit that the structural changes associated with the core fragment in the three dissociation steps are negligible or proportional to each other. From the above discussion a very significant conclusion is drawn at the m.o. level that the protons never get electronically coupled to each other at any stage of dissociation.

We now turn to the problem of ligand based electron transfer in *tris*-bpy complexes of d^6 metal ions. Since the two sets of electron transfers individually conform to the thermodynamics of proton transfer in H_3PO_4 (figure 1), various conclusions drawn in case of the acid apply here also. The structural argument is substantiated by the observation of the reversible to quasireversible nature of the redox processes in cyclic voltammetry. The most important revelation is that the three bpy-centred orbitals remain non-interacting to maintain their identity regardless of the level of reduction, i.e., the electrons get localised on the respective bpy fragments (for spectroscopic evidence of this aspect, see Coombe *et al* 1984). This is the crux of the problem. This makes the series - 1 and 2 - comparable. From figures 1 and 2, we find that the magnitude of the inter-electronic repulsions - a factor mainly responsible in bringing about the difference in the potentials of the two sets of electron transfers - is more or less the same or is proportional for each bpy orbital. This again indicates the non-interacting nature of the three m.o. at all stages of reduction. It may be stated in this connection that the metal mediated splitting of the three ligand centred orbitals has been probably overestimated in the reported semiempirical calculations on these systems (Vlcek

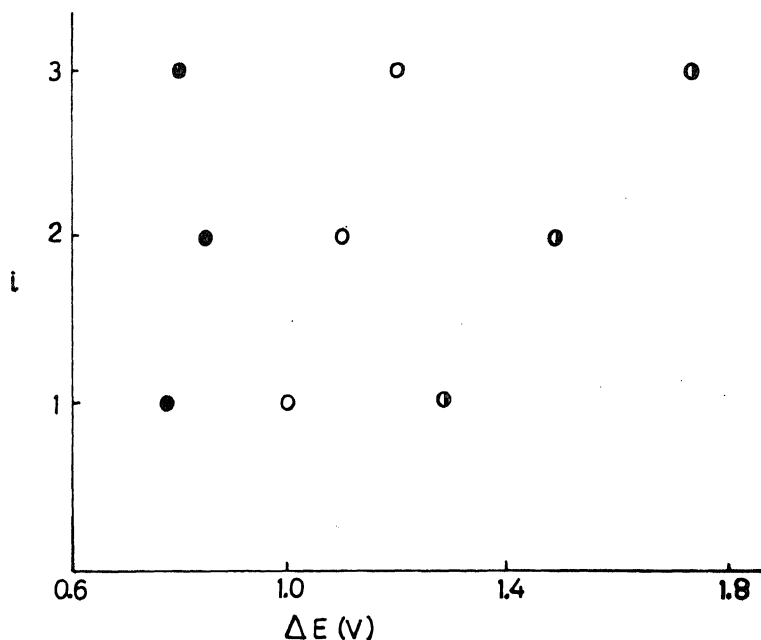


Figure 2. Variation of ΔE , the difference in the potentials of the i th members of the two sets (1a) and (1b), with i , for $Ru(\text{substituted } bpy)_3^{3+}$ [●], $Ir(bpy)_3^{3+}$ [○] and $Cr(o\text{-semiquinone})_3$ [◐].

1982; Yasuhiko *et al* 1984). Similar observations are made in case of the redox series obtained in tris (*o*-semiquinone) chromium(III) complexes (Downs *et al* 1979) (figure 1).

It is worthwhile noting that very recently it has been shown that the thermodynamics of the four-membered electron transfer series obtained for the *bis*-dithiolene and dithiolene-like ligands complexes of d^8 metal ions are similar to that of the proton transfers in pyrophosphoric acid, a tetrabasic acid (Chakravorty 1983). This result together with our present work suggest an interesting possibility of the existence of a proton transfer series corresponding to every electron transfer series from the thermodynamic point of view.

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Some trivalent lanthanide complexes of l-tyrosine hydrazide

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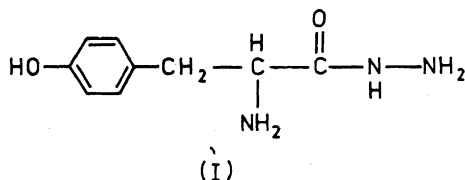
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Abstract. Tyrosine hydrazide (TH) has been found to form complexes of the types $[M(TH)_3Cl_2]Cl$ [$M = La(III), Pr(III), Nd(III)$] and $[M'(TH)_2Cl_2]Cl$ [$M' = Sm(III), Eu(III), Gd(III)$ and $Dy(III)$]. The complexes have been characterized by elemental analysis, molar conductance, magnetic susceptibility, infrared, electronic and PMR spectral studies. The nephelauxetic ratio (β), covalency (δ) and bonding parameter, ($b^{1/2}$) of $[Nd(TH)_3Cl_2]Cl$ have been calculated. Infrared spectral studies reveal that TH acts as a neutral bidentate ligand. Coordination numbers of eight around $La(III)$, $Pr(III)$ and $Nd(III)$ and six around $Sm(III)$, $Eu(III)$, $Gd(III)$ and $Dy(III)$ have been proposed in the complexes.

Keywords. Lanthanide metal complexes; 1-tyrosine hydrazide complexes; synthesis; six and eight-coordinated complexes.

1. Introduction

Considerable interest has recently been evinced in the study of metal complexes of amino-acids containing catecholic or phenolic side chains mainly due to the potentially multidentate ligational behaviour of these amino acids (Birch and Manahan 1967; Weber and Simeon 1971; Gergely *et al* 1971; Vander Helm and Tatsch 1972; McAuliffe and Murray 1973). Work in this area has been stimulated by the implication of metal ions in biological reactions of tyrosine and L- β -(3,4-dihydroxyphenylalanine) (DOPA). This interest has led us to the synthesis and study of a variety of transition metal complexes derived from tyrosine hydrazide, TH (I) and its hydrazones (Rao *et al* 1984, 1985). We have now extended these studies to lanthanide metal complexes and the present paper deals with the syntheses and structural studies of complexes of TH with $La(III)$, $Pr(III)$, $Nd(III)$, $Sm(III)$, $Eu(III)$, $Gd(III)$ and $Dy(III)$.



2. Materials and methods

2.1 Materials

Hydrated lanthanide trichlorides obtained from the Indian Rare Earths Ltd., Kerala, and l-tyrosine hydrazide purchased from M/s Sigma Chemical Company,

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U.S.A., were used as such without further purification. All the other chemicals used in this study were of BDH, AR grade.

2.2 Synthetic outlines

All the complexes were prepared by mixing together hot methanolic solutions of TH (3.75 m mol) and the appropriate metal chloride (1.25 m mol) and stirring the reaction mixture vigorously for ≈ 10 min. The complexes were either precipitated immediately or precipitation was induced by the addition of acetonitrile/diethyl ether. The microcrystalline complexes were filtered, washed with a mixture of acetonitrile and methanol and dried *in vacuo*.

2.3 Analyses of the complexes

The lanthanides were gravimetrically estimated as oxides (Kolthoff *et al* 1963) as well as oxalates after decomposing the organic matter with aqua regia and subsequently with concentrated H_2SO_4 . Chloride was determined gravimetrically as AgCl . Hydrazine was estimated volumetrically after subjecting the complexes to acid hydrolysis. Nitrogen was microanalyzed.

2.4 Physical measurements

Microanalysis was carried out on a Coleman Automatic Analyser. Magnetic susceptibility measurements were made at room temperature on a Cahn-Faraday electrobalance and molar conductance was determined on a WTW conductivity meter. The infrared spectra were recorded as nujol mull on a Perkin-Elmer spectrophotometer, model-621, while the electronic spectra of the complexes in DMF were obtained on a Cary-14 spectrophotometer. PMR spectra were recorded on an FX 90Q JEOL NMR spectrometer.

3. Results and discussion

The analytical data (table 1) of the complexes under present investigation show that TH forms adducts with Ln(III) salts. A 1:3 metal-ligand mole ratio has been observed in the adduct complexes of La(III), Pr(III) and Nd(III) while a 1:2 mole ratio exists in those of Sm(III), Eu(III), Gd(III) and Dy(III) despite the synthesis of all the complexes under similar experimental conditions. This observation is in accordance with the higher coordination numbers expected for the early lanthanide metal ions. All our efforts to isolate the La(III), Pr(III) and Nd(III) complexes with a 1:2 metal-ligand mole ratio resulted in the formation of extremely hygroscopic complexes with indefinite composition leading to irreproducible analytical results presumably due to the presence of varying numbers of solvent molecules.

Based on the fact that TH is reported to form deprotonated complexes with 3d-metal ions owing to the elimination of phenolic protons at $\text{pH} \sim 9.5$ (Chou and McAuliffe 1975), an effort has been made to isolate under high pH conditions, Ln(III) complexes involving the deprotonated ligand, but only the metal hydroxides have been obtained instead of the desired products.

All the $\text{M(TH)}_n\text{Cl}_3$ complexes are stable but become moderately hygroscopic on long exposure to the atmosphere. The complexes are soluble in water, ethanol,

Table 1. Analytical data and general behaviour of Ln(III) complexes of TH.

Complex	Colour	M.P. (°C)	Found (calc.), %				Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)		μ_{eff} (B.M.)
			Metal	Cl	N	N ₂ H ₄			
[La(TH) ₃ Cl ₂]Cl	White	220d	16.68 (16.72)	12.54 (12.81)	14.92 (15.17)	11.42 (11.56)	70.8 ^a	125.5 ^b	Diamag- netic
[Pr(TH) ₃ Cl ₂]Cl	Pale green	242d	16.02 (16.92)	12.41 (12.78)	14.90 (15.13)	11.38 (11.53)	76.7 ^a	118.3 ^b	3.68
[Nd(TH) ₃ Cl ₂]Cl	Pale violet	235d	17.15 (17.20)	12.48 (12.73)	14.69 (15.07)	11.25 (11.48)	88.5 ^a	116.6 ^b	3.89
[Sm(TH) ₂ Cl ₂]Cl	Cream colour	168d	23.06 (23.35)	16.02 (16.45)	12.82 (12.98)	9.73 (9.89)	65.0 ^a	78.9 ^b	1.88
[Eu(TH) ₂ Cl ₂]Cl	White	210d	23.12 (23.47)	16.18 (16.43)	12.71 (12.95)	—	94.4 ^a	76.7 ^b	3.06
[Gd(TH) ₂ Cl ₂]Cl	White	252d	23.96 (24.05)	16.12 (16.27)	12.63 (12.85)	9.62 (9.79)	100.3 ^a	88.5 ^b	7.27
[Dy(TH) ₂ Cl ₂]Cl	White	268d	24.39 (24.66)	15.96 (16.14)	12.57 (12.74)	9.58 (9.71)	102.3 ^a	90.3 ^b	9.47

^aValues in DMF solution; ^bvalues in methanolic solution; d – decomposes.

methanol, DMF and DMSO but are insoluble in non-polar organic solvents like benzene and carbon tetrachloride. The complexes are non-melting and decompose at specific temperatures (table 1). The molar conductance values (table 1) of the complexes in 0.001 M DMF solutions show 1:1 electrolytic behaviour (Geary 1971). A 1:1 electrolytic behaviour of the complexes has been observed even in a poor coordinating solvent like methanol at 10⁻³M concentrations (table 1). This observation prompts us to assume that one of the chloride groups is present outside the coordination sphere of the central metal ion and consequently, the empirical formula of the complexes may be written more precisely as [M(TH)_nCl₂]Cl.

3.1 Magnetic moments

All the complexes in the present study with the exception of the La(III) complex show magnetic moments (table 1) corresponding to the Van Vleck values (Van Vleck and Frank 1929) indicating a little perturbation of 4*f*-orbitals by the ligand fields.

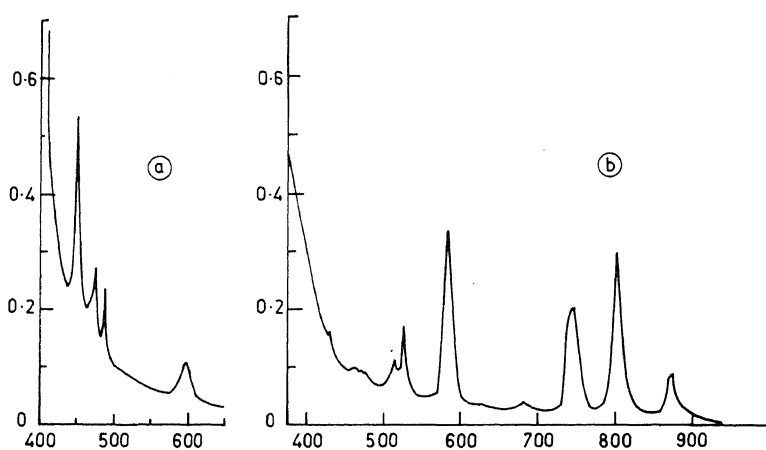
3.2 Electronic spectra

The electronic spectra (table 2) of the Pr(III), Nd(III) and Sm(III) complexes are recorded in 0.02 M DMF solutions and the typical spectra are shown in figure 1. The hypersensitive band (17,125 cm⁻¹) corresponding to the transition ⁴I_{9/2} → ⁴G_{5/2}, ²G_{7/2} in the Nd(III) complex shows significant red shift compared to that of the aquoneodymium complex (Choppin *et al* 1966). The slight shift in such bands has been attributed by Jorgensen (Jorgensen 1957) to the effect of crystal fields upon the interelectronic repulsions among the 4*f*-electrons, i.e., to lowering of the interelectron repulsion parameter in the complex. Further, the shape of the hypersensitive band of the present Nd(III) complex is comparable to that of [Nd(H₂O)₈]³⁺ reported by Karraker (1968) suggesting an eight-coordination.

Table 2. Electronic spectral data of Ln(III) complexes of TH.

Complex	Band maximum (cm ⁻¹)	Assignment	Spectral parameters*
[Pr(TH) ₃ Cl ₂]Cl	16,805	³ H ₄ → ¹ D ₂	
	20,535	→ ³ P ₀	
	21,055	→ ³ P ₁	
	22,220	→ ³ P ₂	
[Nd(TH) ₃ Cl ₂]Cl	11,455	⁴ I _{9/2} → ⁴ F _{3/2}	
	12,470	→ ⁴ F _{5/2}	
	13,370	→ ⁴ F _{9/2}	
	17,125	→ ⁴ G _{5/2} , ² G _{7/2}	$\bar{\beta} = 0.9850$
	19,045	→ ⁴ G _{9/2}	$b^{1/2} = 0.0866$
	19,415	→ ² K _{15/2}	$\delta = 1.522$
	21,060	→ ² G _{9/2}	
	21,185	→ ⁴ G _{11/2}	
[Sm(TH) ₂ Cl ₂]Cl	6420, 6530	⁶ H _{5/2} → ⁶ H _{15/2}	
	7195, 7300	→ ⁶ F _{5/2}	
	8065, 8165	→ ⁶ F _{7/2}	
	9200, 9345	→ ⁶ F _{9/2}	
	10505	→ ⁶ F _{11/2}	
	20835	→ ⁴ I _{11/2}	
	21645	⁴ I _{13/2}	

*Spectral parameters are calculated for hypersensitive transitions, ⁴I_{9/2} → ⁴G_{5/2}, ²G_{7/2}.

**Figure 1.** Electronic spectra of (a) [Pr(TH)₃Cl₂]Cl, and (b) [Nd(TH)₃Cl₂]Cl.

Hence a similar coordination number may be proposed for the present complex. From the β values the covalency parameter (δ) and bonding parameter ($b^{1/2}$) have been determined using the standard procedures (Sinha 1966; Henrie and Choppin 1968). The values of $\bar{\beta}$, which are less than unity, and the positive values of (δ) and $b^{1/2}$ support the idea of a partial covalent bond between the metal and the ligand. A weak covalent bond may similarly be invoked in the analogous Pr(III) and Sm(III) complexes.

3.3 Infrared spectra

The bonding sites of TH involved in coordination with the metal ions have been determined by a careful comparison of the IR spectra of the complexes with the spectrum of tyrosine hydrazide.

The bands due to the -NH stretching frequency in the complexes are often broad, either due to hydrogen-bonding between the anions and the -NH group or due to the overlapping of $\nu(\text{NH})$ and $\nu(\text{OH})$ bands. Hence, no conclusion has been drawn from the shifts in $\nu(\text{NH})$ bands regarding the involvement of the ligand -NH group in bonds with the metal ion.

The IR spectrum of free tyrosine hydrazide shows a band of medium intensity at 1640 cm^{-1} which may be assigned to the >C=O stretching mode (Bontchev *et al* 1981). The insolubility of TH in $\text{HCCl}_3/\text{CCl}_4/\text{CH}_3\text{CN}$ precluded the recording of its spectrum in solution. The above band of TH appears at nearly the same position in all the present complexes indicating the non-involvement of the >C=O group in coordination with the metal ion. Further, the positions of the amide II and amide III bands appearing at 1540 and 1300 cm^{-1} , respectively, in the spectrum of the ligand remain unaffected in the spectra of all the complexes, thus confirming the non-involvement of the >C=O group in coordination. The non-involvement of the >C=O group in the complexes is also shown by their PMR spectra discussed later.

The bands appearing in the spectrum of TH at $1590(s)$, $1100(w)$ and $570(m)\text{ cm}^{-1}$ may be assigned to NH_2 scissoring + C=C stretching, NH_2 wagging and NH_2 rocking modes, respectively (Rao *et al* 1984). These modes appear in the spectra of all the complexes in the regions $1570\text{--}1565$, $1095\text{--}1085$ and $550\text{--}540\text{ cm}^{-1}$ respectively. The negative shifts in all these modes indicate the involvement of both the nitrogen atoms, viz., the amino group nitrogen and the terminal nitrogen of the hydrazide moiety of the ligand in coordination (Inomata *et al* 1974). Further, the bands appearing in the free ligand at 1240 and 650 cm^{-1} , assigned respectively to the OH in-plane and out-of-plane deformation modes of the phenolic -OH group (Inomata *et al* 1974), remain unaltered in the complexes indicating the non-coordination of the phenolic -OH group. The non-ligand bands appearing in the $350\text{--}330\text{ cm}^{-1}$ region in the spectra of all the complexes are tentatively assigned to the $\nu(\text{M-N})$ modes (Charpentier and Moeller 1970; Nagsee *et al* 1977).

3.4 PMR spectra

The PMR spectrum of TH in $\text{DMSO-}d_6$ shows two slightly broad signals centred at $9.10\text{ }\delta$ and $4.03\text{ }\delta$ due to the imino and amino protons of the hydrazide moiety and a doublet with δ values 3.27 and 3.21 owing to the amino protons of the α -carbon atom. The signal due to the imino group of the hydrazide moiety appears at the same position in the spectrum of $[\text{La}(\text{TH})_3\text{Cl}_2]\text{Cl}$ as that in the parent ligand which may be interpreted in terms of the non-coordination of the >C=O group with the metal ion, since its coordination is expected to affect the signal of the adjacent NH group. The signal due to the amino group of the hydrazide moiety undergoes a considerable broadening coupled with a decrease in its intensity to an extent beyond detection as a result of its coordination with La(III) . The doublet due to the amino group on the α -carbon atom is found to be merged into a single peak with a

down-field shift in the La(III) complex, which clearly indicates the coordination of the NH_2 group with the metal ion.

Based on the elemental analyses and various physico-chemical studies, coordination numbers of eight around La(III), Pr(III) and Nd(III) and six around Sm(III), Eu(III), Gd(III) and Dy(III) have been proposed in the present complexes.

Acknowledgements

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Oxidation-reduction electron transfer of tetra-sulphonated phthalocyanine cobalt(II)-apomyoglobin and tetra-sulphonated phthalocyanine iron(II)-apomyoglobin

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Abstract. Studies on electron transfer in (tspc)Co(II)-apoMb and (tspc)Fe(II)-apoMb were carried out as a function of pH by using optically transparent thin layer electrodes. (tspc)Co(II)-apoMb goes to two-stage oxidation-reduction equilibria, whereas, (tspc)Fe(II)-apoMb is stabilized by the protein itself. The mechanism proposed for stabilization of (tspc)Fe(II)-apoMb is the ligand-metal charge transfer from the imidazole of the histidine residue of protein to the central Fe ion of (tspc)Fe(III)-apoMb. The formation of a super-oxide is proposed for the oxygenation of (tspc)Co(II)-apoMb. The reduction potential of (tspc)Co(II)-apoMb $\rightleftharpoons$ (tspc)Co(III)-apoMb, using ferrocene mono carboxylic acid as mediator, is reported, as also the reduction potential for (tspc)Co(II)-apoMb $\rightleftharpoons$ (tspc)Co(I)-apoMb, using Ru(NH₃)₆Cl₃ as mediator. The dependence of $E^{1/2}_{\text{obs}}$ on pH indicates the presence of the ionizable functional groups on the protein, which undergo ionization when the protein changes from the reduced to the oxidised form. The K_{ox} and K_{red} parameters were calculated and are reported here.

Keywords. Oxidation-reduction; electron transfer; (tspc)Co(II)-apoMb.

1. Introduction

The prosthetic group, heme, in hemoglobin and myoglobin is responsible for the transportation of molecular oxygen. Heme binds reversibly with oxygen to catalyse the oxidation of hydrocarbons and to regulate the physiological functions.

Recently many studies have been carried out on hemoglobin and myoglobin by changing their heme site with other macromolecules of iron- and cobalt-containing substituted porphyrins and non-porphyrins. They have shown that the behavior of the modified proteins is similar to that of the native myoglobin and hemoglobin (Przywarska-Boniecka *et al* 1975; Przywarska-Boniecka and Trynda 1978a; Przywarska-Boniecka and Swirska 1980; Kildahl *et al* 1983). These studies were carried out by circular dichroism, Raman spectroscopy and UV-visible difference spectroscopy, which showed that the modified hemoglobin and myoglobin have the capacity to bind reversibly with molecular oxygen.

EPR techniques were used for cobalt and iron tetra-sulphonated phthalocyanine derivatives of myoglobin and hemoglobin to demonstrate their oxygen-binding properties with low-spin metal ion in protein structure (Przywarska-Boniecka and Trynda 1978a; Ruzic *et al* 1982).

X-ray crystallographic studies on the protoporphyrin IX cobalt(II) compounds indicated that these complexes bind with apoproteins in the same way as the heme in hemoglobin, myoglobin and cytochromes (Padlau *et al* 1975).

So far there is very little information on purification and oxidation-reduction electron transfer properties of these modified proteins (Przywarska-Boniecka *et al* 1978b) and this paper describes the studies on the preparation and oxidation-reduction electron transfer of cobalt(II) tetra-sulphonated phthalocyanine apomyoglobin, (tspc)Co(II)-apoMb and iron(III) tetra-sulphonated phthalocyanine apomyoglobin, (tspc)Fe(III)-apoMb, complexes.

2. Experimental

All chemicals used were of reagent grade. NANOpure water was used in all the experiments. pH measurements were made with a radiometer model pH M84 meter connected with a GK231C combination electrode. (tspc)Co(II) and (tspc)Fe(III) were synthesised as described by Weber and Busch (1965). Horse heart myoglobin, type III, was purchased from Sigma chemical company and was converted to apomyoglobin (apoMb) as described earlier by Yonetani (1967) and Breslow *et al* (1967). Concentration of apoMb was determined by apo-heme titration as described by Breslow *et al* (1967).

2.1 Reconstitution of (tspc)Co(II)-apoMb

The solution containing 10 μ M apoMb and 11 μ M (tspc)Co(II) were mixed in 250 ml of 0.1 M sodium phosphate buffer (pH 6). The mixture was stirred for 1 hour in a nitrogen atmosphere at 4°C. The solution was concentrated to 3 ml and passed through a Sephadex G-50 (2.5 $\times$ 45 cm) column, which was equilibrated with 0.1 M sodium phosphate buffer (pH 6) at 4°C. The fractions containing metalloprotein were identified by UV and visible spectroscopy and dialysed against a number of changes of distilled water and finally in 5 mM sodium phosphate buffer (pH 6) at 4°C. The dialysed solution was adsorbed on CM-52, cation exchange column (1.5 $\times$ 10 cm), equilibrated with 5 mM sodium phosphate buffer (pH 6) at 4°C. The column was washed five times with the same buffer. The adsorbed metalloprotein was eluted with a potassium phosphate buffer whose concentration was gradually increased from 5 to 200 mM at pH 6 and temperature 4°C. The fractions containing metalloprotein were concentrated and used for physical studies.

2.2 Reconstitution of (tspc)Fe(II)-apoMb

(tspc)Fe(II)-apoMb was also prepared as described above, except that the (tspc)Fe(III) was reduced to (tspc)Fe(II) with ascorbic acid in 1:1 stoichiometry and purified on a Sephadex G-25 column prior to use.

Electrochemical measurements were made with an optically transparent thin layer electrode (OTTLE) in a non-isothermal configuration as described by Reid *et al* (1982). Electronic absorption spectra were obtained on a Cary-219 spectrophotometer equipped with a thermal isolation accessory and rear beam attenuator and Shimadzu UV-250 recording spectrophotometer.

The solution of (tspc)Co(II)-apoMb was prepared in 0.1 M sodium phosphate buffer. Ru(NH₃)₆Cl₃ ($E^\circ = 50$ mV/NHE, Lim *et al* 1972) was obtained from Alfa and purified by the method of Pladziejewicz *et al* (1973). The purified Ru(NH₃)₆Cl₃

was used as mediator for $(\text{tspc})\text{Co(II)-apoMb} \rightleftharpoons (\text{tspc})\text{Co(I)-apoMb}$ step. Ferrocene mono carboxylic acid ($E^\circ = 530 \text{ mV/NHE}$, Kuwanajn 1977) was obtained from Sigma chemical company and was used as mediator for $(\text{tspc})\text{Co(II)-apoMb} \rightleftharpoons (\text{tspc})\text{Co(III)-apoMb}$ step. These mediators have negligible absorption in the UV-visible range and are taken in 1:10 concentration of the protein. The solution containing protein and mediator (0.5 ml) were electrochemically deoxygenated *in situ* by reduction for 15 min at -360 mV/NHE and subjected to one oxidation-reduction cycle prior to the data collection. The absorbance/potential data were analysed as described by Sailasuta *et al* (1979) with weighted linear least squares fit to the Nernst equation. The mid-point potentials were referenced to the normal hydrogen electrode, NHE, as described by Dutton (1978).

3. Results

The spectra of the purified $(\text{tspc})\text{Co(II)-apoMb}$ and $(\text{tspc})\text{Fe(II)-apoMb}$ are shown in figures 1a and 1b, respectively. The concentration of protein was determined by using the molar absorptivity coefficients reported by Trynda (1983).

The typical spectrum generated in a spectroelectrochemical titration experiment is shown in figure 2a for $(\text{tspc})\text{Co(II)-apoMb} \rightleftharpoons (\text{tspc})\text{Co(III)-apoMb}$ and figure 3a

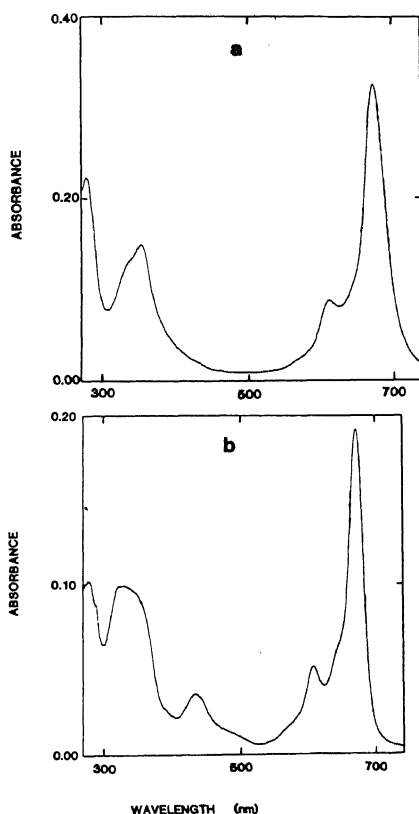


Figure 1. Electronic absorption spectra of (a) purified $(\text{tspc})\text{Co(II)-apoMb}$ ($12.5 \mu\text{M}$), and (b) $(\text{tspc})\text{Fe(II)-apoMb}$ ($6 \mu\text{M}$), in 0.1 M sodium phosphate buffer ($\text{pH } 7$) at 25°C .

for $(\text{tspc})\text{Co(II)}\text{-apoMb} \rightleftharpoons (\text{tspc})\text{Co(I)}\text{-apoMb}$ equilibria. The isosbestic points were obtained at 740, 648, 450, 336 and 290 nm for $(\text{tspc})\text{Co(II)}\text{-apoMb} \rightleftharpoons (\text{tspc})\text{Co(III)}\text{-apoMb}$ and 652, 542 and 368 nm for $(\text{tspc})\text{Co(II)}\text{-apoMb} \rightleftharpoons (\text{tspc})\text{Co(I)}\text{-apoMb}$ equilibria. The equilibria between transparent electrode, mediator and protein were determined at each potential by monitoring the change in absorbance, at 676 nm for $(\text{tspc})\text{Co(II)}\text{-apoMb} \rightleftharpoons (\text{tspc})\text{Co(III)}\text{-apoMb}$, and at 628 nm for $(\text{tspc})\text{Co(II)}\text{-apoMb} \rightleftharpoons (\text{tspc})\text{Co(I)}\text{-apoMb}$. These changes were attained within 30 minutes.

The reduction potentials were obtained from a plot of applied potential, E_{app} , vs. the logarithm of the ratio of concentrations of oxidised to reduced forms of the protein:

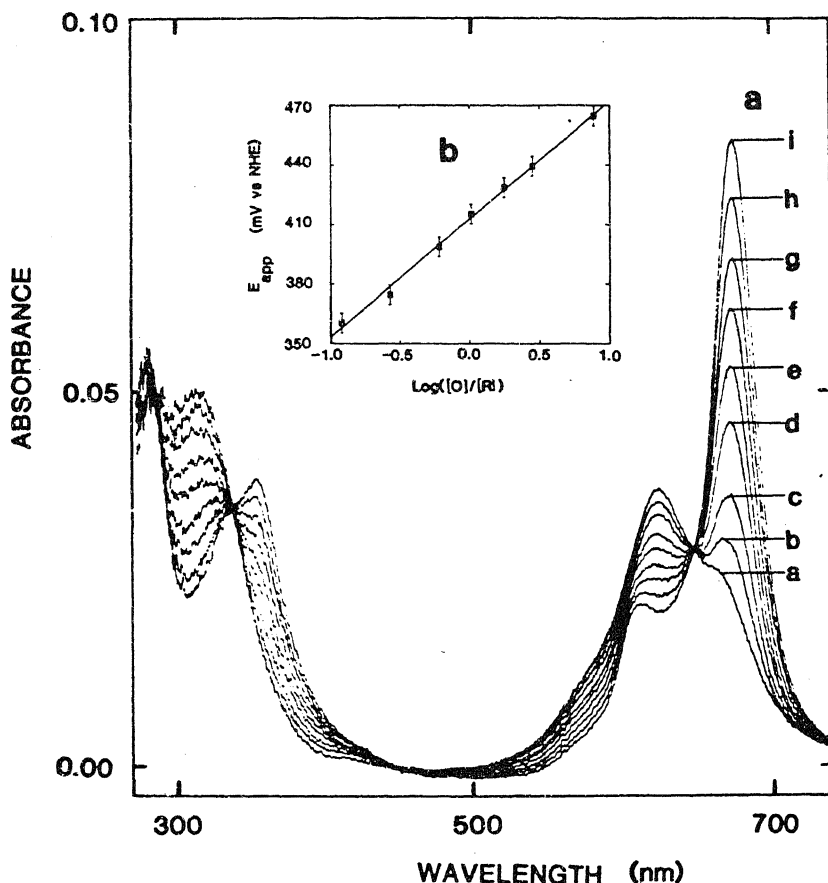


Figure 2. Electrospectrochemical thin layer spectra shows $(\text{tspc})\text{Co(II)}\text{-apoMb} \rightleftharpoons (\text{tspc})\text{Co(III)}\text{-apoMb}$ at different values of applied potential, E_{app} (mV/NHE). $(\text{tspc})\text{Co(II)}\text{-apoMb}$ (160 μM), ferrocene mono carboxylic acid (16 μM), in 0.1 M sodium phosphate (pH 7) at 25°C; (a) 244.2, (b) 360.4, (c) 374.6, (d) 398.7, (e) 415.2, (f) 428.7, (g) 439.4, (h) 464.7, (i) 644.4. The inset shows the Nernst plot calculated by using ΔA_{676} of the main figure. The mid-point potential determined from this analysis is 412.6(1) mV/NHE and the slope is 59.5(2)/pH unit. The error bars are the uncertainty of 0.5 mV in the observed potential.

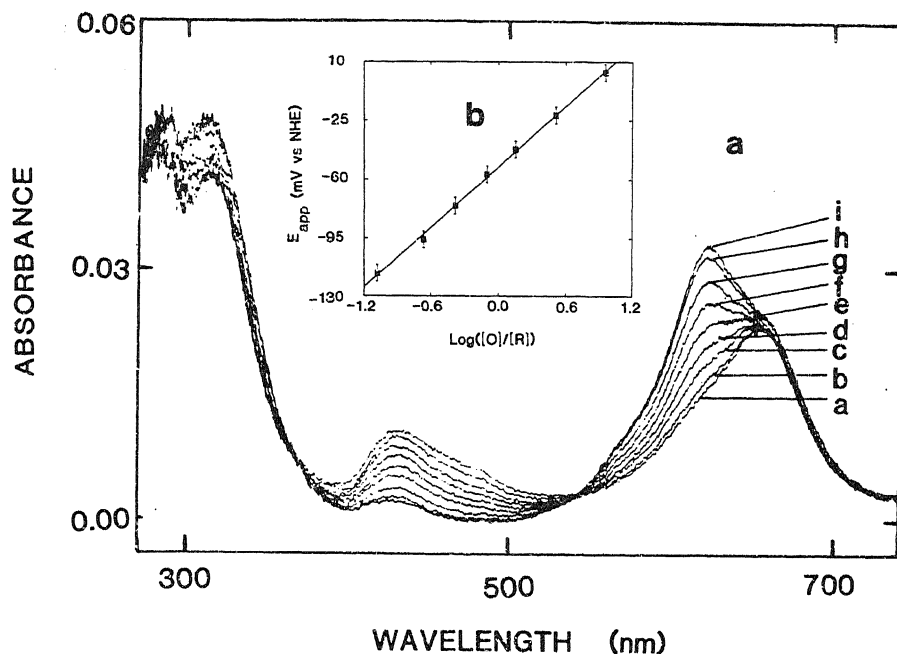


Figure 3. Electrochemical thin-layer spectra shows (tspc)Co(II)-apoMb $\rightleftharpoons$ (tspc)Co(I)-apoMb at different values of applied potential, E_{app} (mV/NHE). (tspc)Co(II)-apoMb (160 μ M), Ru(NH₃)₆Cl₃ (18 μ M), in 0.1 M sodium phosphate (pH 7) at 25°C: (a) -355.6, (b) -116.1, (c) -95.9, (d) -75.7, (e) -56.9, (f) -42.1, (g) -21.9, (h) 3.7, (i) 94.4. The inset shows the Nernst plot calculated by using ΔA_{628} of the above. The mid-point potential determined from this analysis is -52.5(1) mV/NHE and the slope is 59.9(1) mV/pH unit. The error bars are the uncertainty of 0.5 mV in the observed potential.

$$E_{app} = E_{obs}^{1/2} + (RT/nF) \ln ([O]/[R]), \quad (1)$$

where [O] and [R] are the concentrations of oxidized and reduced protein at an applied potential (E_{app}) and was quantitated by measuring the changes in the absorption at 676 nm (figure 2a) for (tspc)Co(II)-apoMb $\rightleftharpoons$ (tspc)Co(III)-apoMb and at 628 nm (figure 3a) for (tspc)Co(II)-apoMb $\rightleftharpoons$ (tspc)Co(I)-apoMb (Dutton 1978). The $E_{obs}^{1/2}$ values reported are the averages of at least three independent runs. The Nernst plot (E_{app} vs. $\log([O]/[R])$) were obtained from these spectrums are shown in figures 2b and 3b for (tspc)Co(II)-apoMb $\rightleftharpoons$ (tspc)Co(III)-apoMb and (tspc)Co(II)-apoMb $\rightleftharpoons$ (tspc)Co(I)-apoMb, respectively. The protein was fully reversible and was cycled between reduced and oxidised states without any detectable change in behavior.

Figures 4a and 4b showed the chemical structure and intramolecular changes during the aerobic reconstitution of (tspc)Co(II)-apoMb and (tspc)Fe(III)-apoMb, respectively.

The effect of pH on the reduction potential of (tspc)Co(II)-apoMb $\rightleftharpoons$ (tspc)Co(III)-apoMb and (tspc)Co(II)-apoMb $\rightleftharpoons$ (tspc)Co(I)-apoMb equilibria are shown in figures 5a and 5b respectively. These data were analysed by

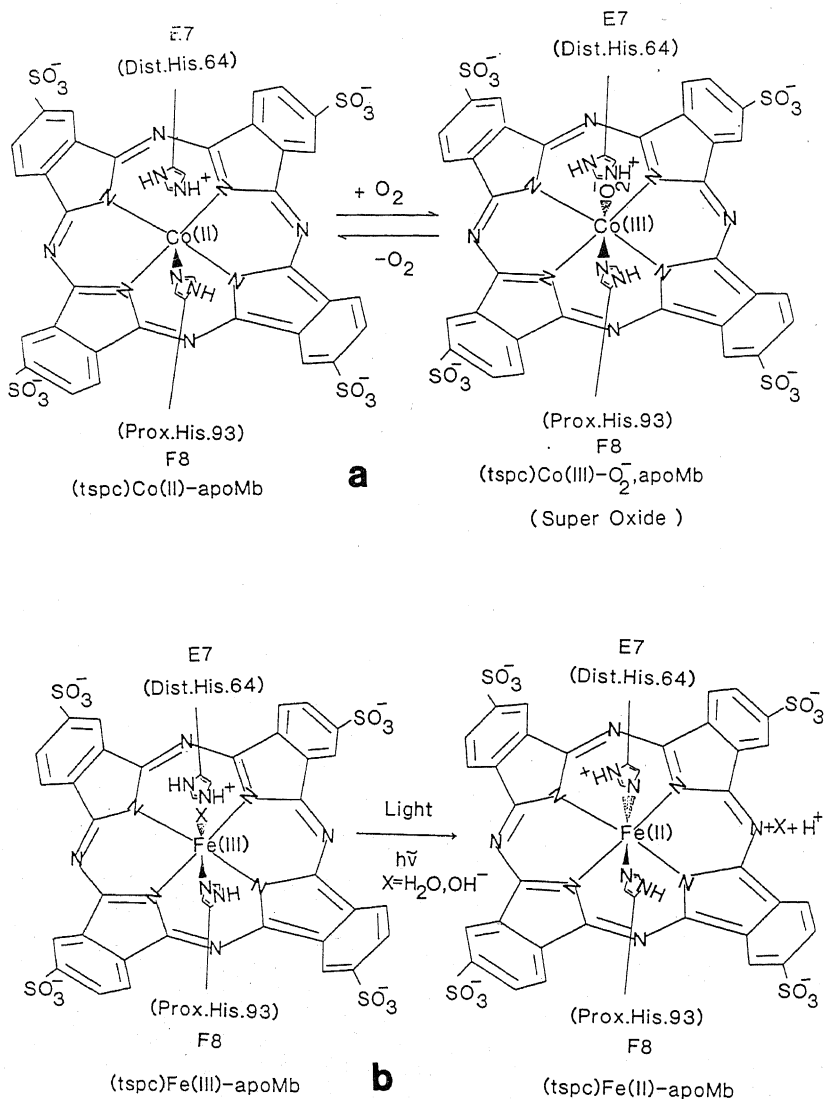


Figure 4. a. Chemical structure and oxygenation of (tspc)Co(II)-apoMb; **b.** Chemical structure and stabilization of (tspc)Fe(II)-apoMb.

the method of Clark (1972) and Ricard *et al* (1972) as described by Moore *et al* (1980) for cytochrome C₅₅₁ by a weighted non-linear least squares fit of the reduction potentials to the relationship:

$$E_{\text{obs}}^{1/2} = E^{\circ} + (RT/2 \cdot 303 nF) \log (K_{\text{red}} + [\text{H}^+]) / (K_{\text{ox}} + [\text{H}^+]), \quad (2)$$

where K_{red} and K_{ox} are the constants in terms of concentration for reduced and oxidised forms of the protein at equilibrium, respectively (Dutton 1978; Reid *et al* 1982). This approach assumes the existence of an ionizable functional group that undergoes a change in pK_a , when protein changes its oxidation states. The data for (tspc)Co(II)-apoMb $\rightleftharpoons$ (tspc)Co(III)-apoMb produce the values of

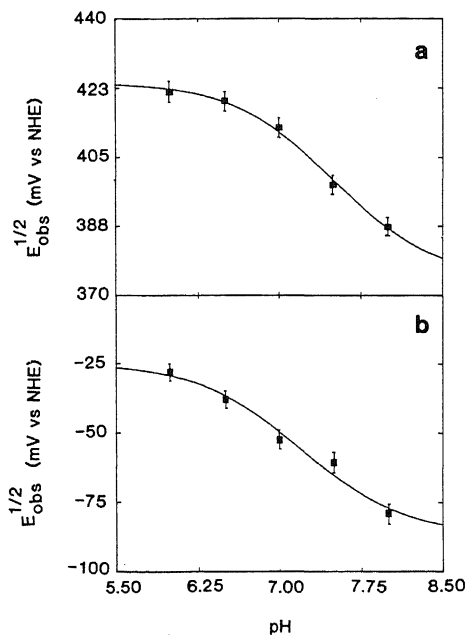


Figure 5. pH dependence of the reduction potentials, the solid lines are the theoretical fit to the data to (2) described in the text. (a) $(tspc)Co(II)-apoMb \rightleftharpoons (tspc)Co(III)-apoMb$ equilibrium, and (b) $(tspc)Co(II)-apoMb \rightleftharpoons (tspc)Co(I)-apoMb$ equilibrium, in 0.1 M sodium phosphate buffer (pH 7) at 25°C.

$K_{ox} = 81$ nM ($pK_{ox} = 7.09$) and $K_{red} = 12$ nM ($pK_{red} = 7.92$) with an E value of 424 mV/NHE. The data for $(tspc)Co(II)-apoMb \rightleftharpoons (tspc)Co(I)-apoMb$ produce the values of $K_{ox} = 210$ nM ($pK_{ox} = 6.68$) and $K_{red} = 19$ nM ($pK_{red} = 7.71$) with an E° of -25 mV/NHE.

The spectra of $(tspc)Co(II)-apoMb$ and $(tspc)Fe(II)-apoMb$ were not significantly affected by change in pH.

4. Discussion

Electrochemical measurements on the $(tspc)Co(II)-apoMb \rightleftharpoons (tspc)Co(III)-apoMb$ equilibrium have yielded the values of the reduction potentials, $E_{obs}^{1/2}$, as 421.5, 419.3, 412.6, 398 and 387.4 mV/NHE at pH 6, 6.5, 7, 7.5 and 8, respectively. The value of $E_{obs}^{1/2}$ (412.6 mV/NHE at pH 7) is greater than the value for the native myoglobin (50 mV/NHE, Antonini *et al* 1964; Brunori *et al* 1971), hemoglobin (150 mV/NHE, Antonini *et al* 1964; Brunori *et al* 1971) and the $(tspc)Co(II) \rightleftharpoons (tspc)Co(III)$ equilibrium (252 mV/NHE, Kundo and Keier 1968). This explains that $(tspc)Co(II)-ApoMb$ has greater affinity towards molecular oxygen and has the ability to oxidise and reduce the other metalloproteins under physiological conditions. Anaerobic electrochemical experiments and the oxygenation and deoxygenation studies reveal that $(tspc)Co(II)-apoMb$ forms its superoxide, $(tspc)Co(III)O_2^-apoMb$, and undergoes deoxygenation after its exposure to the atmospheric oxygen (figure 4a).

Studies on the oxidation-reduction properties of (tspc)Fe(II)-apoMb reveal that this does not get oxidised or reduced after its reconstitution from (tspc)Fe(II) or (tspc)Fe(III) with apomyoglobin. It has been shown that in heme-substituted myoglobin, the distal histidine E7 no. 64, opposite to the iron-linked imidazole of proximal histidine F8 no. 93, stabilizes iron in its reduced form and prevents oxidation (Kagen 1973). On the basis of the ligand-metal charge transfer, the plausible mechanism was proposed and shown in figure 4b.

EPR and spectrophotometric measurements have shown that (tspc)Co(II)-apoMb binds reversibly with molecular oxygen (Ruzic *et al* 1982), whereas (tspc)Fe(II)-apoMb, was stabilised by the ligand charge transfer mechanism from the bulk of the protein to the central metal ion in the protein structure (Przywarska-Boniecka *et al* 1978b).

The values of $E_{\text{obs}}^{1/2}$ for (tspc)Co(II)-apoMb $\rightleftharpoons$ (tspc)Co(I)-apoMb step were -28, -39.9, -52.5, -60.6 and -78.8 mV/NHE at pH 6, 6.5, 7, 7.5 and 8, respectively. The value of $E_{\text{obs}}^{1/2}$ (-52.5 mV/NHE at pH 7) is less than the reduction potentials for myoglobin and haemoglobin and greater than the (tspc)Co(II) $\rightleftharpoons$ (tspc)Co(I) equilibrium (-210 mV/NHE, Kundo and Keier 1968).

Lower reduction potential than that of myoglobin and hemoglobin presumably favours the stabilization of the oxidised form of protein (tspc)Co(II)-apoMb shows that it has the capacity to take or give electrons to the other metalloproteins. This is a typical example and first in the series of myoglobin derivatives, which goes to the two stage oxidation-reduction processes at the physiological conditions. Figures 5a and 5b showed the increase in the reduction potential at the decrease of pH. This may be accounted for the presence of an ionizable functional group on the protein that undergoes a change in protonation when protein changes its oxidation states at various pH values.

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Interaction of metal ions with cytidine and amino carboxylic acids

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Abstract. The interaction of Cu(II), Ni(II), Zn(II), Co(II), Mg(II) and Ca(II) ions with cytidine and amino carboxylic acids (EDTA, NTA and IMDA) in a 1:1:1 ratio have been investigated by potentiometric equilibrium measurements at 35°C and 0.10 M (KNO₃) ionic strength. These investigations were undertaken to assess the influence of the secondary ligands on the structure and stability of the 1:1 metal-cytidine system. The stabilities of ternary and binary complexes are compared and stabilization factors are explained.

Keywords. Cytidine; divalent metal ions; amino carboxylic acids; ternary complexes; stability constants; steric factors.

1. Introduction

The interaction of metal ions with nucleosides and nucleotides, both in binary and ternary systems, have attracted the attention of many scientists throughout the world (Izatt *et al* 1971; Eichhorn 1973; Martin *et al* 1973; Sigel 1973; Taqui Khan and Rabindra Reddy 1973; Marzilli 1977; Martin and Mariam 1979; Rabindra Reddy *et al* 1979; Orenberg *et al* 1980; Rabindra Reddy and Harilatha Reddy 1983). This is mainly due to the fact that metal ions are known to effect the structure of nucleic acids (Eichhorn 1973). Since nucleotides and nucleosides constitute the backbone structure of nucleic acids, any information on the interactions of metal ions with these ligands (nucleosides and nucleotides) is worthwhile. In the present manuscript, ternary complexes of Cu(II), Ni(II), Zn(II), Co(II), Mg(II) and Ca(II) with cytidine and amino carboxylic acids, disodium salts of ethylene diamine tetraacetic acid (Na₂EDTA), nitrilotriacetic acid (NTA) and iminodiacetic acid (IMDA), have been investigated. Earlier work on the ternary complexes of cytidine was confined mainly to Th(IV) and UO₂(II) (Ramalingam and Krishnamoorthy 1982) and EPR and electron absorption studies on the interaction of Cu(II)-glycylglycine complexes (Deshpande *et al* 1983). In a recent article (Rabindra Reddy and Malleswar Rao 1985) the significance of secondary ligands in the structure and stability of metal cytidine complexes in solution has been emphasized. The results obtained from this investigation are compared with literature data to get a clear idea about the influence of secondary ligands on the stabilities of 1:1 metal-ligand complexes. The study of ternary com-

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plexes with diverse groups of secondary ligands, we hope, will lead to a better understanding of the metal-nucleoside interactions in solution.

2. Experimental

Cytidine, IMDA and NTA were obtained from Sigma Chemical Company (USA) and Na₂EDTA was obtained from Glaxo Laboratories, India. For every titration, fresh solid ligands were weighed out into the reaction cell to avoid possible hydrolysis. Transition and alkaline earth metal ions [Cu(II), Ni(II), Zn(II), Co(II), Mg(II) and Ca(II)] were of AnalaR grade and were standardized volumetrically by titration with the disodium salt of ethylene diamine tetraacetic acid in the presence of a suitable indicator as outlined by Schwarzenbach (1957). Carbonate free sodium hydroxide was prepared by the method of Schwarzenbach and Biedermann (1948).

The experimental method employed consisted of potentiometric titration of the ligands with standard sodium hydroxide solution, in the absence and presence of the above mentioned metal ions. The ionic strength was kept constant by using 0.10 M (KNO₃) as the supporting electrolyte and relatively low concentrations of the ligand and metal ion (1×10^{-3} M). During the course of the titration a stream of nitrogen was passed over the solution to eliminate the adverse effect of atmospheric carbon dioxide.

All measurements were made at $35^\circ \pm 0.1^\circ\text{C}$. Equimolar ratios of metal and ligands were employed in the investigation. Further details are given in our earlier work (Rabindra Reddy *et al* 1984).

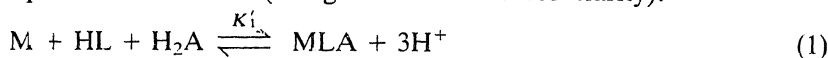
3. Calculations

3.1 Dissociation constants

The acid dissociation constants of the primary ligand cytidine and the secondary ligands Na₂EDTA, NTA and IMDA were calculated by the usual algebraic method.

3.2 Formation constants

To calculate the stability constants of the ternary complexes of Cu(II), Ni(II), Zn(II), Co(II), Mg(II) and Ca(II) with cytidine and Na₂EDTA in a 1:1:1 ratio the following equations were used (charges are omitted for clarity):



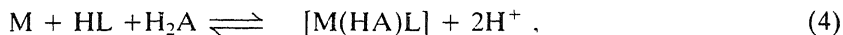
together with the related equilibria



$$K_{MLA}^M = \frac{T_M - [M]}{[M][L][A]}. \quad (3)$$

Equations (1)–(3) were also employed to calculate the stability constants of the ternary complexes of Cu(II), Ni(II), Zn(II) and Co(II) with cytidine-NTA and cytidine-IMDA.

For the ternary complexes of Mg(II) and Ca(II) with cytidine-NTA and cytidine-IMDA in a 1:1:1 ratio, (4)–(6) used were in the buffer region between $m = 0$ and $m = 2$.



together with related equilibria



$$K_{M(HA)L}^M = \frac{T_M - [M]}{[M][L][A]} , \quad (6)$$

In the buffer region between $m = 2$ and $m = 3$ the following equations were employed:



$$K_{MLA}^{M(HA)L} = \frac{T_M - [M]}{[M][A]} , \quad (9)$$

In (8) and (9) 'M' equals M(HA)L. For (1)–(9), HL = monoprotonated cytidine, A = Na₂EDTA or NTA or IMDA (secondary ligands), T_M = total metal ion species present in solution.

The detailed calculations of these constants are described in our earlier work (Rabindra Reddy and Malleswar Rao 1985).

4. Results

The proton dissociation constants of the ligands cytidine, EDTA, NTA and IMDA are presented in table 1.

4.1 Metal:cytidine:Na₂EDTA system (1:1:1)

The mixed ligand titration curve of Cu(II)-cytidine-Na₂EDTA given in figure 1 (c) shows an inflection at $m = 3$ (where m is moles of base added per mole of metal ion), indicating simultaneous formation of a 1:1:1 mixed ligand complex in the entire buffer region between $m = 0$ and $m = 3$. The constant K_{MLA}^M was calculated with the help of (3). Similar trends were observed for other systems studied and the corresponding stability data are presented in table 2.

Table 1. Acid dissociation constants of ligands.
Temperature = 35°C; $\mu = 0.10 \text{ mol dm}^{-3}$ (KNO₃).

Ligand	pK_a	pK_{2a}	pK_{3a}	pK_{4a}
Cytidine	4.15 ± 0.04			
Na ₂ EDTA			6.12 ± 0.03	9.92 ± 0.03
NTA		2.35 ± 0.05	9.45 ± 0.05	
IMDA	2.45 ± 0.04	9.27 ± 0.04		

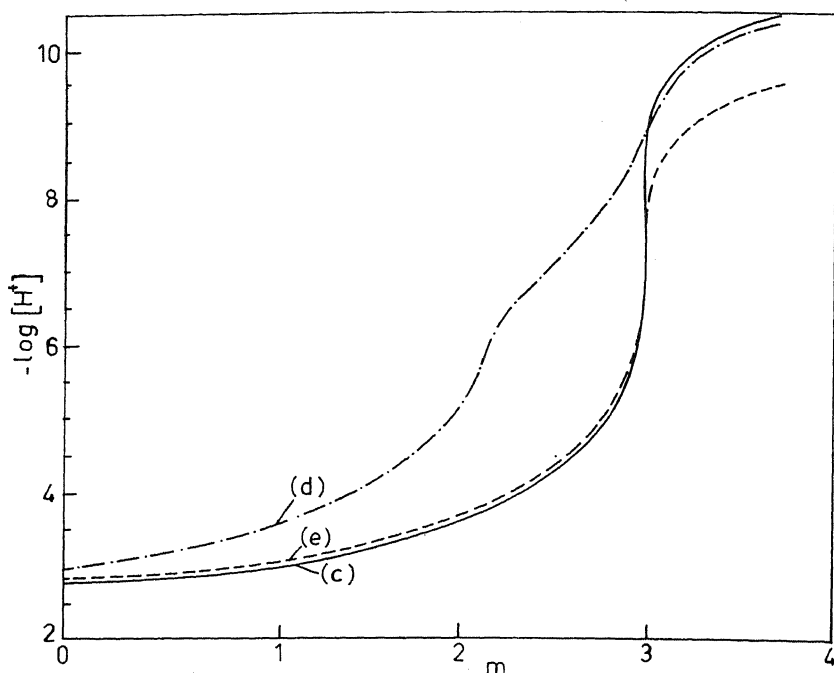


Figure 1. Potentiometric titration curves for Cu(II) : cytidine : Na₂EDTA, Cu(II) : cytidine : NTA and Mg(II) : cytidine : NTA in a 1:1:1 ratio at 35°C and 0.10 M (KNO₃) ionic strength. c = Cu(II) : cytidine : Na₂EDTA; d = Mg(II) : cytidine : NTA; e = Cu(II) : cytidine : NTA; m = moles of base added per mole of metal ion.

Table 2. Stability constants* of the ternary complexes of cytidine with Na₂EDTA in a (1:1:1) ratio.

Temperature = 35°C; $\mu = 0.10 \text{ mol dm}^{-3}$ (KNO₃)

Metal ion (II)	Metal:cytidine† (1:1) K_{ML}^M	Metal:Na ₂ EDTA (1:1) K_{MA}^M	Metal:cytidine:Na ₂ EDTA (1:1:1) K_{MLA}^M
Cu	3.19	13.80	18.59
Ni	2.94	13.45	17.93
Zn	2.60	13.34	17.62
Co	2.74	13.39	17.78
Mg	2.42	9.43	13.98
Ca	2.47	10.18	14.69

*The constants are accurate upto ± 0.05 ;

†The values are from Khan and Raju (1981).

4.2 Metal:cytidine:NTA systems (1:1:1)

The mixed ligand titration curve of Cu(II) with cytidine and NTA in a 1:1:1 ratio is given in figure 1 (e), resulting in an inflection at $m = 3$, indicating the simultaneous formation of a 1:1:1 mixed ligand complex in the entire buffer region between $m = 0$ and $m = 3$. The constant K_{MLA}^M was calculated with the help of (3). Similar

results were obtained for Ni(II), Zn(II) and Co(II) and the constants are listed in table 3.

However, in the case of other metal ions [Mg(II) and Ca(II)], an inflection was obtained at $m = 2$ [figure. 1(d)] indicating the formation of a monoprotonated complex in the region between $m = 0$ and $m = 2$. The constant $K_{MLA}^{M(HA)L}$ was also calculated in the buffer region between $m = 2$ and $m = 3$ with the help of (9). All the constants thus calculated are listed in table 3.

4.3 Metal:cytidine:IMDA system (1:1:1)

This system is exactly similar to the metal:cytidine:NTA system. The constants thus calculated are presented in table 4.

5. Discussion

The dissociation constants of various ligands are listed in table 1. In tables 2, 3 and 4 the stability constants of the binary and ternary complexes are compiled. Although the stability constants for the interaction of Cu(II), Ni(II), Zn(II), Co(II), Mg(II) and Ca(II) with amino carboxylic acids are available in the

Table 3. Stability constants* of the ternary complexes of cytidine with NTA in a (1:1:1) ratio.

Temperature = 35°C; $\mu = 0.10 \text{ mol dm}^{-3}$ (KNO₃)

Metal ion (II)	Metal:NTA (1:1)			Metal:cytidine:NTA (1:1:1)		
	K_{MHA}^M	K_{MA}^{MHA}	K_{MA}^M	$K_{M(HA)L}^M$	$K_{MLA}^{M(HA)L}$	K_{MLA}^M
Cu			11.82			15.86
Ni			11.20			15.25
Zn			10.91			15.16
Co			10.77			15.06
Mg	3.94	6.72		8.43	5.95	
Ca	3.79	6.45		8.28	6.07	

*The constants are accurate up to ± 0.04 .

Table 4. Stability constants* of the ternary complexes of cytidine with IMDA in a (1:1:1) ratio.

Temperature = 35°C; $\mu = 0.10 \text{ mol dm}^{-3}$ (KNO₃)

Metal ion (II)	Metal:IMDA (1:1)			Metal:cytidine:IMDA (1:1:1)		
	K_{MHA}^M	K_{MA}^{MHA}	K_{MA}^M	$K_{M(HA)L}^M$	$K_{MLA}^{M(HA)L}$	K_{MLA}^M
Cu			10.28			15.18
Ni			8.17			13.20
Zn			7.24			12.80
Co			6.92			12.59
Mg	2.71	2.65		8.21	3.30	
Ca	2.42	1.74		7.78	2.51	

*The constants are accurate up to ± 0.04 .

literature, we have remeasured these constants as it is preferable to determine the binary and ternary constants under identical experimental conditions. Otherwise, the experimental differences might show up in $\Delta \log K$ values, which are the differences between the overall stability constants of both 1:1:1 ternary stability constants and corresponding 1:1 binary constants leading to errors in interpretation. However, our values agree well with those reported in the literature (Rajan and Martell 1964).

In table 5 are given the $\Delta \log K$ values for various metal ligand systems. It can be seen from the tables that the $\Delta \log K$ values are positive for all the systems studied which indicates that the formation of ternary complexes is preferred to that of binary complexes. These enhanced stabilities of ternary systems are due to the tendency of secondary ligands to form chelate rings. When the $\Delta \log K$ values of these systems are compared (EDTA, NTA and IMDA) it is found that the metal-cytidine-IMDA system has more positive $\Delta \log K$ values compared to other systems. These trends can be explained on the basis of steric factors. The less bulky IMDA will have least steric hindrance compared to NTA and EDTA resulting in the formation of more stable ternary complexes in solution. Based on our observation we proposed a tentative structure for metal-cytidine-IMDA system

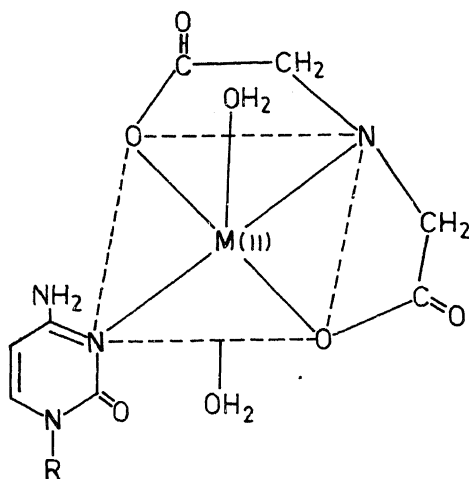


Figure 2. Tentative structure of 1:1:1 M(II) : cytidine : IMDA. R = Ribose.

Table 5. $\Delta \log K$ values for various metal-ligand systems in solution. Temperature = 35°C; $\mu = 0.10 \text{ mol dm}^{-3} (\text{KNO}_3)$.

Metal ion (II)	Metal:cytidine:IMDA (1:1:1)	Metal:cytidine:Na ₂ EDTA (1:1:1:1)	Metal:cytidine:NTA (1:1:1)
Cu	+1.71	+1.60	+0.85
Ni	+2.09	+1.54	+1.11
Zn	+2.96	+1.68	+1.65
Co	+2.93	+1.65	+1.48
Mg	+3.08	+2.13	+2.07
Ca	+2.89	+2.04	+2.02

(figure 2). It is of interest and importance to compare the $\Delta \log K$ values obtained for the interaction of metal-cytidine with biologically important secondary ligands—histidine and histamine (Rabindra Reddy and Malleswar Rao 1985) with corresponding values with amino carboxylic acids. The metal-cytidine-histidine and metal-cytidine-histamine form more stable complexes as is evident from their more positive $\Delta \log K$ values in spite of the fact that the amino carboxylic acids have larger numbers of donor groups. These results clearly suggest that the stacking interactions, which are expected to occur between two aromatic moieties of the ligands, seem to be the most effective phenomenon that contribute to the extra stabilization found in ternary complexes. This observation is in line with the results obtained earlier on the nucleoside complexes (Rabindra Reddy *et al* 1985) and their related systems (Rabindra Reddy and Madhusudhan Reddy 1986).

Acknowledgements

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Reactions of dialkoxynaphthalenes with cyclic α,β -unsaturated acids

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Abstract. Synthetically useful substituted hexahydrobenzofluoren-11-ones and tetrahydropentalenonaphthalen-10(H)-ones are prepared in one step by the reaction of cyclic α,β -unsaturated acids, namely, 1-cyclohexene-1-carboxylic acid and 1-cyclopentene-1-carboxylic acid, with substituted dialkoxynaphthalenes in the presence of polyphosphoric acid. The stereochemistry at the C/D ring junction is determined from the ^1H NMR and by decoupling experiments.

Keywords. 1-Cyclohexene-1-carboxylic acid; 1-cyclopentene-1-carboxylic acid; hexahydrobenzofluorenone; tetrahydropentalenonaphthalenone.

1. Introduction

In a project for the synthesis of polycyclic compounds, we investigated the reaction of dialkoxynaphthalenes with cyclic α,β -unsaturated acids, such as 1-cyclohexene-1-carboxylic acid (A) and 1-cyclopentene-1-carboxylic acid (B) (Wheeler and Lerner 1956) in the presence of polyphosphoric acid (PPA) at 90–95°C. The products isolated after column chromatography were identified as hexahydrobenzofluoren-11-one and tetrahydropentalenonaphthalen-10(H)-one derivatives. Similar types of compounds have been reported as intermediates for the synthesis of C-nor- and C-nor-D-homosteroids (Eglinton *et al* 1956). The methods hitherto available for the synthesis of the above are elaborate and inconvenient. We describe here a simple one-step synthesis giving about 40 to 50% yields of the above compounds.

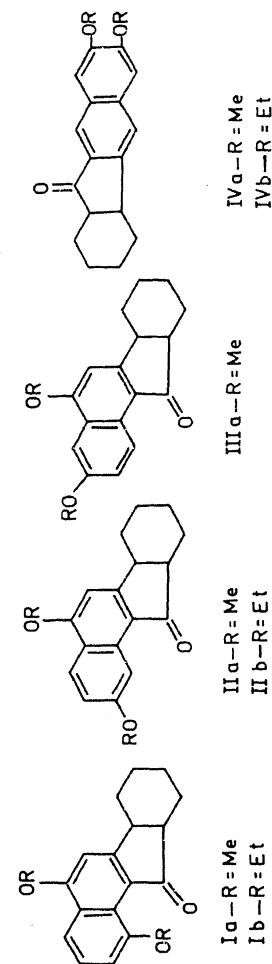
2. Results and discussion

1,5-Dimethoxynaphthalene with acid (A) afforded 1,5-dimethoxy-6b,7,8,9,10,10a-hexahydro-11H-benzo(a) fluoren-11-one (Ia) in the presence of PPA. The spectral data are given in table 1.

Theoretically, a number of structures are possible for the product, depending on whether a Friedel-Crafts acylation has occurred first followed by cyclisation or a Michael type addition has taken place followed by ring closure (Chart 1).

Out of these possible structures the linear structure (I'a) is ruled out on the basis of the UV spectrum of Ia (table 1) which supports the angular structure as the data are similar to those of the known angular structures (Moffatt 1966). The structure I'a is ruled out on the basis of ^1H NMR data (table 1), since the C_6 proton in Ia appears at δ 6.72 and in the alternate structure I'a it would have appeared

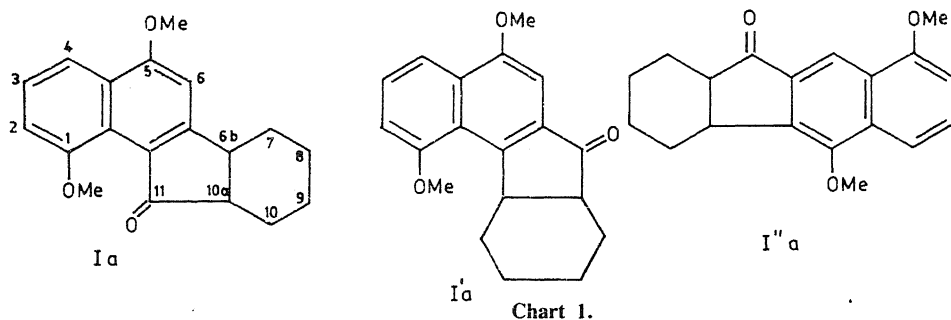
* To whom all correspondence should be addressed.



Dialkoxy-naphthalene used	Compound number	Eluting solvent a:b*	m.p. (°C)	Molecular formula	Analysis (%)		Spectral data
					Calcd	(Found)	
1,5-	Ia	40:60	119-20	$\text{C}_{19}\text{H}_{20}\text{O}_3$	77.0 (76.8)	6.8 (6.8)	UV $\lambda_{\text{max}}^{\text{MeOH}}$ (log ϵ): 233 (4.37); 253 (4.33); 316 (3.88); 338 (3.89) nm. IR (Nujol) ν_{max} : 1700 (>C=O); 1590, 1510, 840 (ar) cm^{-1} . NMR (CDCl_3) δ : 1.15-2.5 (8H, <i>m</i> , CH_2 -7,8,9,10); 2.7-3.0 (1H, <i>q</i> , C_{10}H); 3.15-3.5 (1H, <i>q</i> , C_{6}H); 4.0 (6H, <i>s</i> , two- OCH_3); 6.72 (1H, <i>s</i> , C_6H); 7.0 (1H, <i>d</i> , <i>J</i> = 8 Hz, C_2H); 7.3 (1H, <i>t</i> , C_3H); 7.88 (1H, <i>d</i> , <i>J</i> = 8 Hz, C_4H).
	Ib	60:40	110-11	$\text{C}_{21}\text{H}_{24}\text{O}_3$	77.8 (77.6)	7.4 (7.3)	IR (Nujol) ν_{max} : 1700 (>C=O); 1580, 1520, 1480 (ar) cm^{-1} . NMR (CDCl_3) δ : 1.25-2.5 (14H, <i>m</i> , two $-\text{CH}_3$, CH_2 -7,8,9,10); 2.8-3.0 (1H, <i>q</i> , C_{10}H); 3.1-3.4 (1H, <i>q</i> , C_{6}H); 4.2 (4H, <i>q</i> , two $-\text{OCH}_3$); 6.7 (1H, <i>s</i> , C_6H); 7.0 (1H, <i>d</i> , <i>J</i> = 8 Hz, C_2H); 7.3 (1H, <i>t</i> , C_3H); 7.88 (1H, <i>d</i> , <i>J</i> = 8 Hz, C_4H).
1,6-	IIa	40:60	128-29	$\text{C}_{19}\text{H}_{20}\text{O}_3$	77.0 (77.3)	6.8 (6.6)	UV $\lambda_{\text{max}}^{\text{MeOH}}$ (log ϵ): 239 (4.41); 325 (4.00) nm. IR (Nujol) ν_{max} : 1700 (>C=O); 1640, 1600, 1530 (ar) cm^{-1} . NMR (CDCl_3) δ : 1.15-2.4 (8H, <i>m</i> , CH_2 -7,8,9,10); 2.7-3.0 (1H, <i>q</i> , C_{10}H); 3.3-3.5 (1H, <i>q</i> , C_{6}H); 4.0 (6H, <i>d</i> , two $-\text{OCH}_3$); 6.7 (1H, <i>s</i> , C_6H); 7.15 (1H, <i>dd</i> , <i>J</i> = 2 Hz, <i>J</i> = 8 Hz, C_3H); 8.1 (1H, <i>d</i> , <i>J</i> = 8 Hz, C_4H); 8.56 (1H, <i>d</i> , <i>J</i> = 2 Hz, C_1H).

1,7-	IIb	70:30	124-25	$C_{21}H_{24}O_3$	77.8 (77.7)	7.4 (7.5)	UV λ_{max}^{MeOH} (log ϵ): 239 (3.85), 257 (3.80); 328 (3.38) nm. IR (Nujol) ν_{max} : 1680 ($>C=O$); 1640, 1600, 1520 (ar) cm^{-1} . NMR ($CDCl_3$) δ : 1.3-2.4 (14H, m, two $-CH_3$, CH_2 -7,8,9,10); 2.6-3.0 (1H, q, $C_{10a}H$); 3.2-3.55 (1H, q, $C_{6a}H$); 4.25 (4H, q, two $-OCH_3$); 6.7 (1H, s, C_6H); 7.15 (1H, dd, $J = 2$ Hz, $J = 8$ Hz, C_3H); 8.2 (1H, d, $J = 8$ Hz, C_4H); 8.55 (1H, d, $J = 2$ Hz, C_1H).
	IIIa		184-85	$C_{19}H_{20}O_3$	77.0 (77.3)	6.8 (6.6)	IR (Nujol) ν_{max} : 1685 ($>C=O$); 1590, 1520, 1480 (ar) cm^{-1} . NMR ($CDCl_3$) δ : 1.12-2.35 (8H, m, CH_2 -7,8,9,10); 2.68-2.98 (1H, q, $C_{10a}H$); 3.35-3.56 (1H, q, $C_{6a}H$); 4.0 (6H, d, two $-OCH_3$); 6.72 (1H, s, C_6H); 7.3 (1H, dd, $J = 2$ Hz, $J = 8$ Hz, C_3H); 7.57 (1H, d, $J = 2$ Hz, C_4H); 9.03 (1H, d, $J = 8$ Hz, C_1H).
2,3-	IVa	10:90	158-59	$C_{19}H_{20}O_3$	77.0 (76.9)	6.8 (6.7)	UV λ_{max}^{MeOH} (log ϵ): 264.5 (4.33); 307 (3.81) nm. IR (Nujol) ν_{max} : 1680 ($>C=O$); 1620, 1500, 1480 (ar) cm^{-1} . NMR ($CDCl_3$) δ : 1.1-2.5 (8H, m, CH_2 -1,2,3,4); 2.7-3.0 (1H, m, $C_{11a}H$); 3.6-3.85 (1H, m, $C_{10a}H$); 4.0 (6H, d, two $-OCH_3$); 7.12 (1H, s, C_5H); 7.2 (1H, s, $C_{10}H$); 7.5 (2H, s, C_6 and C_9H).
	IVb	10:90	164-65	$C_{21}H_{24}O_3$	77.8 (77.9)	7.4 (7.3)	IR (Nujol) ν_{max} : 1680 ($>C=O$); 1620, 1520, 1480 (ar) cm^{-1} . NMR ($CDCl_3$) δ : 1.0-2.35 (14H, m, two $-CH_3$, CH_2 -1,2,3,4); 2.65-3.0 (1H, m, $C_{11a}H$); 3.65-3.95 (1H, m, $C_{10a}H$); 4.2 (4H, q, two $-OCH_2$); 7.2 (1H, s, C_5H); 7.3 (1H, s, $C_{10}H$); 7.6 (2H, s, C_6 and C_9H).

* a = Petroleum ether (b.p. 60-80°); b = benzene.



downfield due to the anisotropic effect of the carbonyl group (Merchant and Upasani 1981). 1,5-Diethoxynaphthalene reacted similarly to give Ib (table 1 for spectral data).

The reaction of 1,5-dimethoxynaphthalene with acid (B) in presence of PPA yielded 1,5-dimethoxy-7,8,9,9a-tetrahydro-pentaleno[2,1-a]naphthalen-10(6bH)-one (Ic) (spectral data in table 2).

The structure Ic is in full agreement with the spectral data. 1,5-Diethoxynaphthalene reacted similarly with acid (B) to yield Id.

Similarly, 1,6-dimethoxy-(diethoxy)-naphthalene reacted with acid (A) to afford 2,5-dimethoxy-(diethoxy)-6b,7,8,9,10,10a-hexahydro-11H-benzo(a)-fluoren-11-one (IIa-b).

In the above structures, the ring D is fused *cis* to ring C as the *cis* fusion is most favoured thermodynamically (March 1977). This fact is supported by the ^1H NMR spectra and the decoupling experiments.

The ^1H NMR data of IIa is given in table 1. The J values are found to be 6.6, 6.1 and 8.5 Hz for the 6b proton and 6.6, 6.9 and 6.5 Hz for the 10a proton. The J value 6.6 which is the same in both the cases corresponds to that for the methine protons, and is less than 8 Hz. Hence, the two rings are *cis* fused. The rings are constantly flipping, thus changing the environments of the methine protons from axial to equatorial and vice-versa (more than 10^3 times per second). Hence the net result will be the average.

The possibility for the *trans* fusion can be ruled out as in this case the methine protons would have to be *trans* (March 1977) (axial-axial only) with each other and the J_{10a-6b} would have been above 8 Hz. Decoupling experiments confirm *cis* fusion. Irradiation at 1.3 ppm resulted in the collapse of the multiplet for H-6b into a doublet with J around 6.6 Hz. The ^{13}C NMR spectrum values are given below as a matter of interest.

^{13}C NMR of IIa – 21.8 (*t*, C-9), 22.14 (*t*, C-8), 23.2 (*t*, C-7), 30.38 (*t*, C-10), 39.17 (*d*, C-10a), 48.31 (*d*, C-6b), 55.44 (*s*, OCH_3), 55.86 (*s*, OCH_3), 98.72 (*d*, C-3), 102.98 (*d*, C-6), 117.87 (*d*, C-4), 119.93 (*s*, C-4a), 121.99 (*s*, C-11b), 124.12 (*d*, C-1), 132.7 (*s*, C-6a), 160.8 (*s*, C-5), 161.8 (*s*, C-11a), 164.5 (*s*, C-2), 207.03 (*s*, C-11).

Heating 1,6-dimethoxy-(diethoxy)-naphthalene with acid (B) in the presence of PPA yielded 2,5-dimethoxy-(diethoxy)-7,8,9,9a-tetrahydro-pentaleno[2,1-a]naphthalen-10(6bH)-one (IIc-d).

For this compound, two sets of J values were obtained, namely 2.6, 8.5, 6.2 Hz for the 6b proton and 1.8, 9.2, 6.2 Hz for the 9a proton. The J value 6.2 which is the

Table 2 (Contd.)

1,7-	IIIb	158-59	$C_{18}H_{18}O_3$	76.6 (76.5)	6.4 (6.3)	IR (Nujol) $\nu_{\max}$: 1680 ($>C=O$); 1580, 1510 (ar) cm^{-1} . NMR ($CDCl_3$) δ : 1.12-2.3 (6H, <i>m</i> , CH_2 -7,8,9); 3.0-3.25 (1H, <i>q</i> , $C_{9a}H$); 3.6-3.85 (1H, <i>q</i> , $C_{6a}H$); 4.0 (6H, <i>d</i> , two $-OCH_3$); 6.8 (1H, <i>s</i> , C_4H); 7.35 (1H, <i>dd</i> , $J = 2$ Hz, C_2H); 7.55 (1H, <i>d</i> , $J = 2$ Hz, C_4H); 9.05 (1H, <i>d</i> , $J = 8$ Hz, C_1H).
2,3-	IVc	20:80	$C_{18}H_{18}O_3$	76.6 (76.8)	6.4 (6.1)	UV $\lambda_{\max}^{MeOH}$ (log ϵ): 224 (4.34); 254 (4.38); 263 (4.35); 309 (3.92) nm. IR (Nujol) $\nu_{\max}$: 1680 ($>C=O$); 1620, 1520 (ar) cm^{-1} . NMR ($CDCl_3$) δ : 1.1-2.3 (6H, <i>m</i> , CH_2 -1,2,3); 3.0-3.4 (1H, <i>m</i> , $C_{10a}H$); 3.75-4.0 (1H, <i>m</i> , $C_{3a}H$); 4.1 (6H, <i>d</i> , two $-OCH_3$); 7.2 (1H, <i>s</i> , C_1H); 7.35 (1H, <i>s</i> , C_9H); 7.6 (2H, <i>s</i> , C_5 and C_8H).
	IVd	10:90	$C_{20}H_{22}O_3$	77.4 (77.6)	7.1 (7.2)	IR (Nujol) $\nu_{\max}$: 1700 ($>C=O$); 1620, 1520 (ar) cm^{-1} . NMR ($CDCl_3$) δ : 1.0-2.3 (12H, <i>m</i> , two $-CH_3$, CH_2 -1,2,3); 3.0-3.4 (1H, <i>s</i> , $C_{10a}H$); 3.75-4.0 (1H, <i>m</i> , $C_{3a}H$); 4.32 (4H, <i>q</i> , two $-OCH_3$); 7.25 (1H, <i>s</i> , C_4H); 7.35 (1H, <i>s</i> , C_9H); 7.6 (2H, <i>s</i> , C_5 and C_8H).

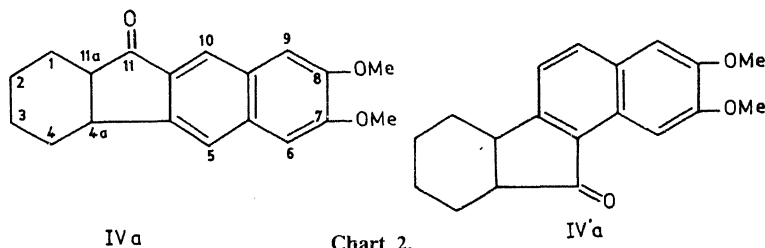
* a = Petroleum ether (b.p. 60-80°); b = benzene.

same must be the coupling constant for the methine proton. This value is less than 8 Hz and hence the rings C/D are *cis* fused with each other. Decoupling experiments confirm *cis* fusion. Irradiation at 1.9 ppm resulted in the collapse of the multiplet at 3.75 into a doublet with $J = 6.5$ Hz, which is the coupling constant for the methine protons. The ^{13}C NMR values are given below as a matter of interest:

^{13}C NMR of IIc – 24.36 (*t*, C-8), 30.5 (*t*, C-9), 32.5 (*t*, C-7), 44.33 (*d*, C-9a), 52.96 (*d*, C-6b), 55.48 (*s*, OCH_3), 55.88 (*s*, OCH_3), 99.15 (*d*, C-3), 103.04 (*d*, C-6), 117.96 (*d*, C-4), 120.04 (*s*, C-4a), 124.0 (*d*, C-1), 124.13 (*s*, C-10b), 132.04 (*s*, C-6a), 161.05 (*s*, C-5), 162.33 (*s*, C-10a), 164.62 (*s*, C-2), 208.54 (*s*, C-10).

When 1,7-dimethoxynaphthalene and 2,3-dialkoxynaphthalenes were reacted with acids (A) and (B) compounds IIIa to IVd were isolated in about 40% yields. The structures of the compounds were assigned on the basis of spectral and analytical data (tables 1 and 2).

2,3-Dimethoxynaphthalene reacted with acid (A) under the above mentioned conditions to give 7,8-dimethoxy-1,2,3,4,4a,11a-hexahydro-11H-benzo(b)fluoren-11-one (IVa) instead of the expected benzo(a)fluorenone. Its spectral data is given in table 1.



Of the possible structures, only structure IVa is in agreement with the NMR spectral evidence. In the NMR spectrum the aromatic protons at C-6 and C-9 appear as a two-proton singlet, whereas the C_5 and C_{10} protons are observed as two different singlets. The singlet at $\delta 7.2$ (attributed to C-10 proton) is shifted downfield due to the anisotropic effect of the carbonyl group, whereas in the alternate structure IV'a an AB pattern would have been observed for C_5 - C_6 protons along with two singlets and the proton at C-1 would have been shifted downfield due to the anisotropic effect of the carbonyl group. 2,3-Diethoxynaphthalene reacted similarly to give IVb.

2,3-Dialkoxynaphthalene reacts with acid (B) to yield 6,7-dialkoxy-2,3,3a,10a-tetrahydropentaleno[1,2-b]naphthalen-10(1H)-one (IVc-d).

All the above substituted hexahydrobenzofluorenones and pentalenonaphthalenones gave crystalline 2,4-dinitrophenylhydrazones derivatives.

3. Experimental

All melting points reported here are uncorrected values IR spectra were recorded on a Perkin-Elmer spectrophotometer. The UV spectra were recorded on a Shimadzu-240 spectrophotometer. The NMR spectra were recorded on a 60 MHz Varian instrument. Chemical shifts are quoted in δ values relative to tetramethyl-

silane (TMS) as internal standard. The homogeneity of compounds was ascertained by TLC on silica gel G plates, and spots were developed in an iodine chamber. Neutral alumina was used for column chromatography.

3.1 Reaction of dialkoxynaphthalene with cyclic α, β -unsaturated acids (A and B)

General procedure: Dialkoxynaphthalene (0.01 mole) and cyclic α, β -unsaturated acid (0.02 mole) were heated in the presence of polyphosphoric acid [prepared from phosphorus pentoxide (10 g) and phosphoric acid (5 ml) preheated at 100°C for 0.5 hr]. The reaction mixture was kept at 90–95°C for a further 3 hr with occasional shaking. It was cooled and decomposed with ice water and left overnight. It was then extracted with chloroform. The chloroform layer was washed with saturated sodium hydrogen carbonate, water and dried over anhydrous sodium sulphate. The solvent was removed by distillation and the dark mass obtained was chromatographed over neutral alumina. Elution with appropriate solvent afforded the respective compounds (tables 1 and 2).

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Experiments with flowing gases in an open photoacoustic cell[†]

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Abstract. A simple gas-microphone photoacoustic cell is described in which there is no sizable loss of signal on opening the cell to the atmosphere or even under conditions of gas flow. Results obtained under different rates of flow of gases and chopping frequencies are reported. Except for carbon black, the photoacoustic signal is found to be independent of flow-rate for all the solid substances studied.

Keywords. Photoacoustic spectroscopy; open photoacoustic cell; flowing gases.

1. Introduction

The versatility of the photoacoustic (PA) technique for studying several phenomena is by now well-documented (Rosencwaig 1980; Ganguy and Rao 1981; Tam 1986). When gas-microphones are used as the detector, it is assumed that the cell should be closed as otherwise the flow of heat to the gas phase from the solid following a non-radiative de-excitation will not result in an increase in pressure. Efforts have been made, however, to construct open PA cells so that the ranges of application of the PA effect may be further extended (Dioszeghy *et al* 1985; Kanstad and Nordal 1978). These cells have limited applications. We have exploited the fact that when a PA cell is connected to the atmosphere by a tube, the fraction of transmitted acoustic wave depends on the dimensions of the tube. By a proper choice of the diameter, length and wall thickness of the capillary such that the acoustic impedance of the capillary is increased, a simple PA cell may be constructed in which there is no sizable loss of photoacoustic signal at ordinary chopping frequencies (f), even though the cell is open to the atmosphere, or more interestingly, when a gas is flowing through the cell. In this communication we describe the cell used by us and the results obtained for various solid samples under different gas flow conditions.

2. Experimental

The cell used by us earlier (Somasundaram and Ganguly 1984) has been modified as shown in figure 1. The arms of the glass capillaries could be varied in order to operate at various f . Glass stopcocks at the end of these arms allowed the cell to be

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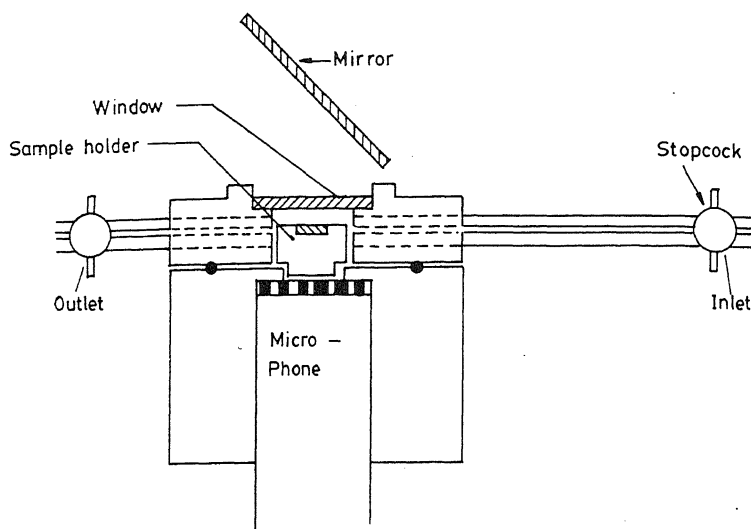


Figure 1. Schematic drawing of the open PA cell used for gas-flow studies.

closed or opened to the atmosphere. The capillaries used in these experiments were of 0.5 mm internal diameter and 2.5 mm wall thickness. Gases could be passed through these capillaries. In order to achieve high flow-rates and at the same time retain the signal strength, we have made the gas-inlet arm 12.5 cm and gas-outlet arm 4.5 cm in length. Flow-rates as high as 2 cc/sec could be achieved without affecting the signal to noise ratio. At higher flow-rates ~ 6 cc/sec or more, there is considerable noise within the cell, associated with the vibrations and rattling of the loosely mounted sample holder and sample. The length of the gas phase between the sample and the window is 3.5 mm and the internal diameter of the cell is 12 mm. The volume within the cell is ~ 0.3 cc so that at the rates of 2 cc/sec the entire volume of the gas in the cell would have been swept out within the chopping period for $f \sim 6.7$ Hz. The microphone used was General Radio 1961-1 inch electret condenser microphone with a flat frequency response between 5–15,000 Hz. Nitrogen gas was used for the gas flow experiments with the flow-rates being measured by a soap bubble flow meter. The lock-in-amplifier, illuminating source, chopper etc. were the same as that described earlier by Ganguly and Rao (1981) and Somasundaram and Ganguly (1984).

3. Results and discussion

We show in figure 2a the changes in the PA signal (I_{PA}) from a flat single crystal of graphite at various chopping frequencies when the cell is closed, open and when nitrogen gas is passing through the cell at 1.2 cc/sec. The behaviour is similar even if the intensity of the illuminating source is varied by a factor of 40. I_{PA} is inversely related to f when the cell is closed, for the whole frequency range studied (6–300 Hz). We have shown in figure 2b the changes in I_{PA} when various arms are opened or closed. We see that for $f \geq 20$ Hz, I_{PA} is hardly changed under the

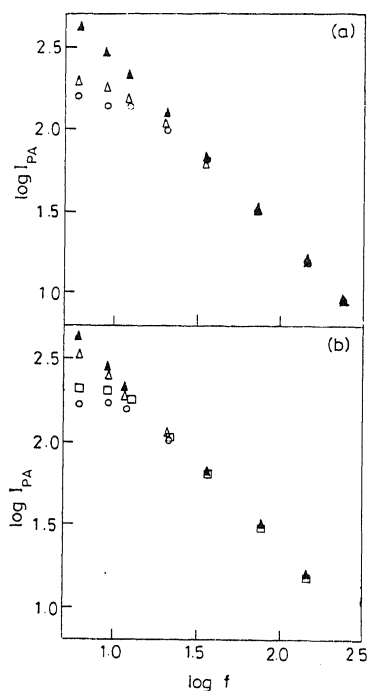


Figure 2. (a) Variation of I_{PA} with f for a single crystal of graphite using white light for illumination under various conditions. Inlet arm length ~ 12.5 cm, outlet arm ~ 4.5 cm. ($\blacktriangle$): cell closed; ($\triangle$): cell open with a gas flow (1.2 cc/sec) and ($\circ$): cell open with no gas flow. (b) Variation of I_{PA} with f for the same conditions as (a). ($\blacktriangle$): both arms closed; ($\triangle$): inlet arm open; ($\square$): outlet arm open and ($\circ$) both arms open.

various conditions, at lower values of f , however, I_{PA} is considerably reduced. At these lower f I_{PA} seems to be proportional to a factor $[1 - (B/l_1 + B/l_2)]$ where l_i are the lengths of the capillary arms ($1/l_i = 0$ when an arm is closed) and B is a constant for each frequency. It is interesting to note that when a gas is passing through the cell, there is a slight increase in I_{PA} at low frequencies, which is close to the value obtained when the inlet arm is closed. There is also considerable change in the phase of the signal. A complete theoretical analysis of this aspect is being further pursued. We note that one has to consider whether the acoustic losses in the capillaries are adiabatic or isothermal in nature (Kinsler and Frey 1950). In general the former is obtained when the diameter of the tube is $> 2.14/(f)^{1/2}$ (in cm) and the latter when the diameter is $< 0.214/(f)^{1/2}$ (in cm). Since the length of the gas phase in the cell is 3.5 mm, the adiabatic condition seems to be fulfilled in the cell only for $f > 37$ Hz. In the capillary there could be isothermal or adiabatic conditions depending on the chopping frequency.

The other aspect is that even under gas flow conditions there is no change in amplitude of I_{PA} for various values of f . In order to understand this aspect further, we have studied the influence of flow-rate on the PA signal generated from various powdered as well as flat solid samples. The changes in I_{PA} from a single crystal of graphite at $f = 6.2$ Hz for two intensities (one being 40 times greater than the other) are shown in figure 3. At this f an equivalent volume of the entire gas in the cell

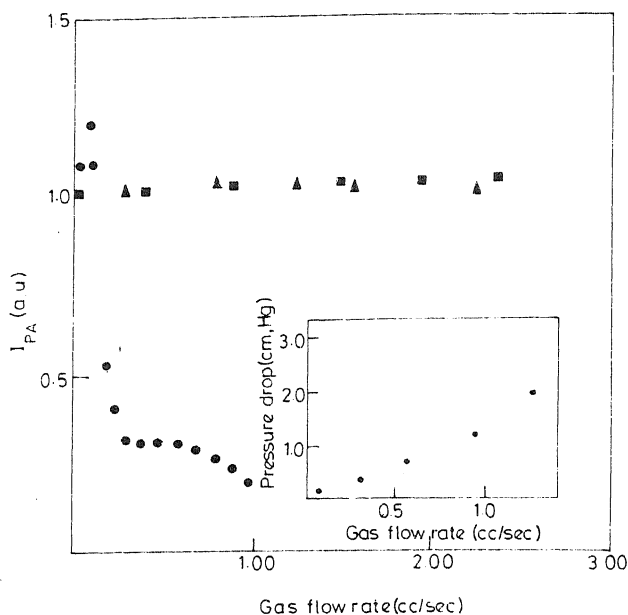


Figure 3. Variation of I_{PA} with gas flow-rate. I_{PA} is normalised to unity for no gas flow conditions. (■) & (▲) for single crystals of graphite using white light. (●) for carbon black powder. I_{PA} corresponding to (▲) when gas flow is zero is nearly the same as (●) but is 40 times larger than that corresponding to (■). Inset shows the measured pressure drop in a mercury manometer for various gas flow rates.

may be displaced during the chopping period for flow-rates ~ 2 cc/sec. The length of the gas phase is moreover nearly equal to the value at which a maximum in I_{PA} is expected from our earlier studies (Ganguly and Somasundaram 1987) at this chopping frequency ($l_g \sim 1.0$ mm at 6.2 Hz). We see no decrease in the PA intensity even at the highest flow-rates. The slight increase may be accounted for the increase in the pressure within the cell. The changes in pressure within the cell was measured by a manometer attached to the cell, after the set of experiments were over. This value of pressure (in cm of Hg) for various gas flow-rates is given in the inset of figure 3. Similar results were obtained with other flat solids such as amorphous selenium deposited on teflon, CdS single crystals etc. as well as various powders such as a-Se, chromia-alumina catalyst. The only exception is, however, with carbon black where there is a marked change in the PA amplitude as a function of flow-rate as shown in figure 3. There is an increase in I_{PA} for small flow-rates followed by a rapid decrease. This behaviour is quite reversible with respect to flow-rate. At high flow-rates I_{PA} seem to be roughly inversely related to the flow-rate. At all flow-rates I_{PA} is however related inversely to f .

The present study throws up some questions which does not seem to be expected from some of the presently accepted theories of the PA effect (Rosencwaig and Gersho 1976). Carbon black is often used as a model substance. The very different behaviour of carbon black does not seem to be related simply to its thermal properties. All the other substances which include high surface area catalysts which have different thermal diffusivities show quite different behaviour. When the gas is

flowing through the cell, part of the heat given up to the gas phase must be carried out of the cell and hence there should be a reduction in I_{PA} with increasing flow-rate accompanied by a marked f dependence. In other words, under gas flow conditions there would be a decrease in the thermal diffusion length and according to the Rosencwaig-Gersho theory there should be a decrease in I_{PA} since it is proportional to the thermal diffusion length. It is therefore surprising that there is no dependence of I_{PA} from fiat bulk single crystal of graphite on the flow-rate even at $f = 6.2$ Hz when $l_g \sim 3.5$ mm is sizably less than $2\pi\mu_g$ (the value at which thermal waves are nearly attenuated in the gas phase). This behaviour does not depend upon the location of the microphone, temperature and cell design. So a jet of gas entering the cell may be made to impinge directly on the sample or other parts of the cell without affecting the results. This behaviour does not seem to be related to the thermal properties of the solid or the powder-gas composite as we have found similar behaviour with a wide range of solids. Further study is now in progress in areas such as study of catalysts under catalytic conditions (Somasundaram and Ganguly 1987), transition from lamellar to turbulent flow etc.

4. Conclusion

The above data clearly demonstrate that a truly open photoacoustic gas-microphone cell may be used at rather high flow-rates of gas through the cell. Thus PA effect may now be extended to several areas such as spectroscopy of catalysts under catalytic conditions, the study of flowing systems as in effluents from reactors, gas-chromatograms, exhausts etc. The transition from lamellar to turbulent flow may perhaps be fruitfully studied by the technique.

Acknowledgement

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Electrochemical phase formation studies of mercury on glassy carbon

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Abstract. The electrochemical phase formation (ECPF) of mercury in the underpotential (UPD) region was studied using cyclic voltammetry on a glassy carbon substrate. The UPD peak, conspicuous by its absence on the fresh glassy carbon electrode in the first cycle, is formed in the second and subsequent cycles reaching a full monolayer coverage over a few cycles. The characterization of the monolayer peak by the theoretical models suggested for linear sweep conditions showed that the UPD of mercury follows progressive nucleation-growth kinetics. The nucleation parameter and nucleation-growth rate constant were calculated.

Keywords. Electrochemical phase formation; glassy carbon; cyclic voltammetry; underpotential region; nucleation parameter; nucleation-growth rate constant.

1. Introduction

The electrochemical phase formation (ECPF) of mercury on a glassy carbon electrode (GCE) in the bulk deposition region was investigated by potentiostatic, galvanostatic and single and double potential step methods (Gunawardena *et al* 1982). An additional stripping peak was observed at more positive potentials to bulk stripping peak, during their cyclic voltammetric studies of mercury on pyrolytic graphite (Marcos 1975). Based on the empirical correlation between underpotential shift (ΔE_p) and the difference in work functions of substrate and depositing metal (Kolb *et al* 1974) the additional peak was qualitatively identified to be due to the stripping of underpotentially deposited mercury. Similar qualitative correlation was arrived using glassy carbon as electrode material (Kiekens *et al* 1983).

Recently a few criteria were laid down for the underpotentially deposited (UPD) peaks obtained in linear sweep experiments that can distinguish the kinetics of ECPF via adsorption or nucleation growth (Bosco and Rangarajan 1981). In our previous communications (Jaya *et al* 1984, 1985) dealing with the determination of mercury by linear sweep anodic stripping voltammetry (LSASV) on glassy carbon, it was noted that the stripping signal increases with each plating and stripping cycle indicating progressive activation of GCE to facilitate the deposition of mercury. The present investigations are therefore undertaken with a view to understand the ECPF of mercury.

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2. Experimental

The experiments were carried out in 0.5 M sulphuric acid solutions, prepared by diluting 98% sulphuric acid (BDH, AR) with water. Mercury (II) nitrate (0.1 M) was added to the 0.5 M sulphuric acid supporting electrolyte solution to obtain the required concentration of mercury. A conventional glass electrolysis cell with provision for deaeration with N_2 gas was used. The working electrode was a glassy carbon electrode (Tokai & Co., 3 mm dia) pressure fitted into a teflon holder. The auxiliary electrode was a platinum foil of large area $\sim 6 \text{ cm}^2$. The reference electrode was a normal calomel electrode with a luggin probe positioned at $\sim 1 \text{ mm}$ from the electrode surface. All potentials were expressed with reference to NCE. The glassy carbon electrode was polished with emery papers of increasing fineness (1/0 to 4/0) and then rinsed with water, acetone, ethanol and water again.

A Wenking (Model LB 75 M) potentiostat coupled with a Wenking scan generator (Model VSG 72) was used for controlling the potential. A digilog XY-2000 recorder was used for recording *I-E* curves.

3. Results and discussion

3.1 Response characteristics of fresh GCE surface

The electrochemical behaviour of mercury on GCE was studied in solutions of 10^{-2} M mercury(II) in 0.5 M sulphuric acid. The polarization is effected by triangular scans of potential beginning with cathodic followed by anodic sweeps. The cathodic scan was reversed during the initial stages of crystallization (Fletcher *et al* 1983). The results of such experiments are given in figure 1. It is clear from curve A, figure 1, that the response of the system is distinctly different in the first and subsequent triangular scans (curves B, C & D). The features noted in the first triangular scan are:

- a) a rapid rise in current recorded on forward scan once nucleation begins,
- b) a cathodic current maximum results immediately on reversal of the scan direction,
- c) appearance of a characteristic cross-over loop,
- d) a single anodic stripping peak, and
- e) the conspicuous absence of the peak at 0.36 V during cathodic scan of curve A which appears in subsequent scans.

These features indicate that the deposition of mercury follows 3-D nucleation and subsequent grain growth (Fletcher *et al* 1983; Gunawardena *et al* 1982). The behaviour of mercury on GCE during successive scans (after complete stripping of the deposited mercury at 1.0 V for 2 min prior to each scan), in the potential range 1.0 to 0.22 V is shown in curves A, B, C and D of figure 1. It is clear from these triangular scans that, unlike the response for the first scan, a new deposition peak appears at more positive potentials (0.36 V) compared to the equilibrium reversible potential of Hg(II)/Hg(0) , viz., 0.33 V. This new peak increases with each successive scan and reaches saturation beyond the 7th scan. The quantity of the charge passed under the peak at 0.36 V in various scans due to the deposition of

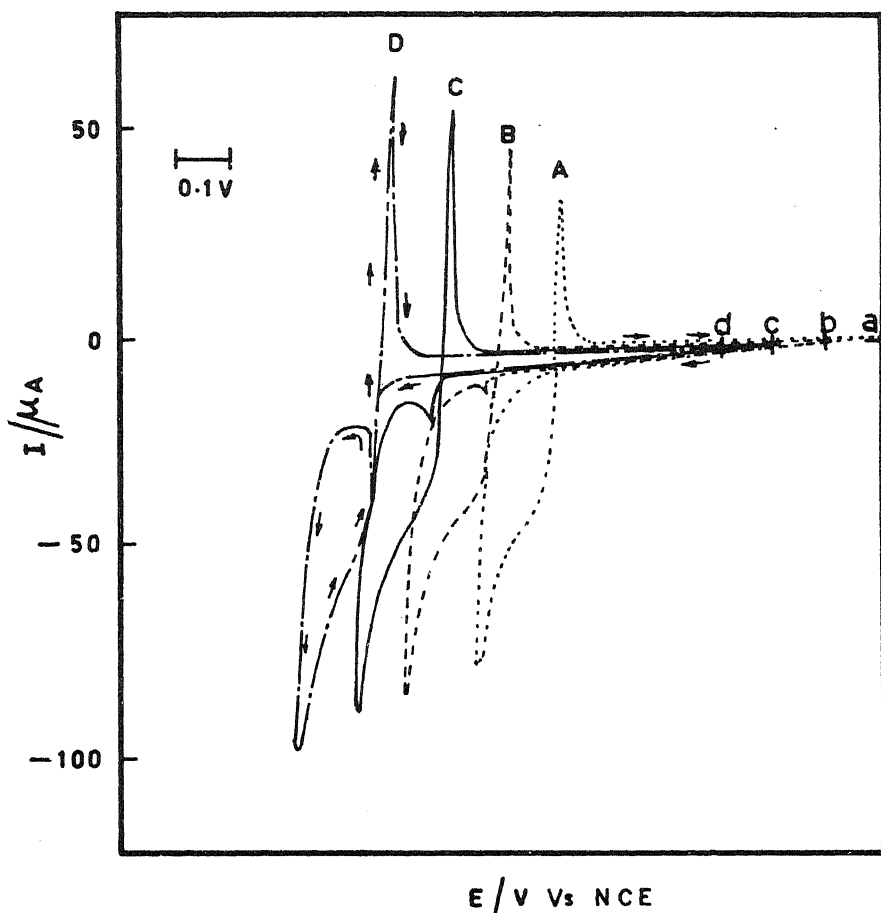


Figure 1. *I-E* curves obtained using triangular scans of potential at 6 mV/s for the deposition of 10^{-2} M mercury(II) nitrate in 0.5 M sulphuric acid in the potential scan range of 1.0 to 0.22 V vs. NCE on glassy carbon in successive scans. Curves A, B, C and D are for 1, 2, 3 and 4th scan, respectively. a, b, c and d represent starting points for curves A, B, C and D respectively (The complete stripping of mercury is ensured before the start of each scan.)

mercury is computed and listed in table 1. Further, this new peak was not due to the reduction of Hg(I) to Hg(0) as the reversible potential for such redox reactions was found to be 0.530 V vs NCE. The standard reduction potentials of the Hg(II)/Hg(I) and Hg(I)/Hg(0) couples were 0.920 and 0.789 V vs NHE or 0.640 or 0.509 V vs NCE respectively (Latimer 1956).

3.2 Identification of the deposition peak occurring at 0.36 V

The peak currents obtained at various sweep rates (ν) bear a linear relationship with ν indicating that the deposition peak occurring at 0.36 V arises due to the surface reaction and not bulk deposition (as i_p vs $\nu^{1/2}$ is expected for bulk deposition) (Birss and Wright 1982).

The adatoms are arranged on the substrate so as to satisfy the requirements of

Table 1. Quantity of charge passed during the deposition of mercury at 0.36 V.

Triangular scan number	Quantity of charge passed 0.36 V vs NCE ($\mu\text{C}/\text{cm}^2$)
1	—
2	95.32
3	272.09
4	353.72
5	383.20
6	442.15
7	471.63
8	471.80

the nature of the chemical valence of surface atoms and adatoms (Furuya and Moto 1979). This concept allows one to arrive at a charge of $500 \mu\text{C}/\text{cm}^2$ ($2 \times 250 \mu\text{C}$) assuming overlap of two orbitals of mercury with one orbital each of carbon. This calculation presupposes the availability of one orbital of carbon to be overlapped by bivalent mercury recognizing the wide prevalence of chemically bound single -OH groups to each carbon atom (Jankowska *et al* 1981). It may be remarked here that, as the presence of =O groups attached to carbon is also known (Jankowska *et al* 1981), the size requirements preclude the presence of one mercury atom over one carbon atom throughout the monolayer. On the other hand, the presence of one mercury atom over one carbon atom at lower coverages cannot be ruled out. In the present case, the saturation coverage is $\sim 500 \mu\text{C}/\text{cm}^2$ indicating that the full monolayer is formed beyond the 7th scan. It may be noted that the corresponding monolayer stripping is not seen during anodic scan. However, when cyclic voltammograms are run by restricting the cathodic potential limit to positive values to the bulk deposition of mercury, it is seen that UPD mercury strips at the same potential as that of the bulk, i.e., at 0.40 V (cf. figure 2), thus suggesting the merger of the monolayer stripping peak with the bulk stripping peak. Further, the deposition and dissolution process of mercury in the UPD region is irreversible as the deposition and stripping peaks of mercury are unsymmetrical over the potential axis in the entire sweep rate range studied. From the sweep rate dependence experiments, it is seen that $\Delta E_{1/2}$ (peak width at half height in nondimensional units) value for both the cathodic (0.36 V) and the anodic (0.40 V) dissolution peaks reaches a value of 0.60 at higher sweep rates. The number of electrons involved during deposition and subsequent dissolution of mercury was calculated to be 2 from $\Delta E_{1/2}$ value as described elsewhere (Bosco and Rangarajan 1981). The peaks appearing at 0.36 and 0.40 V are thus confirmed as being due to deposition/dissolution of submonolayer or monolayer amounts of mercury(II) on GCE. The presence of the UPD peak in 2nd to 7th scan did not alter the deposition characteristics of mercury on GCE in the bulk deposition region listed above. The continued presence of a surface growth loop and a current maximum on reversal of cathodic scan suggest 3-D nucleation and growth processes are still operative (Fletcher *et al* 1983). This is in contrast to the earlier observations obtained during

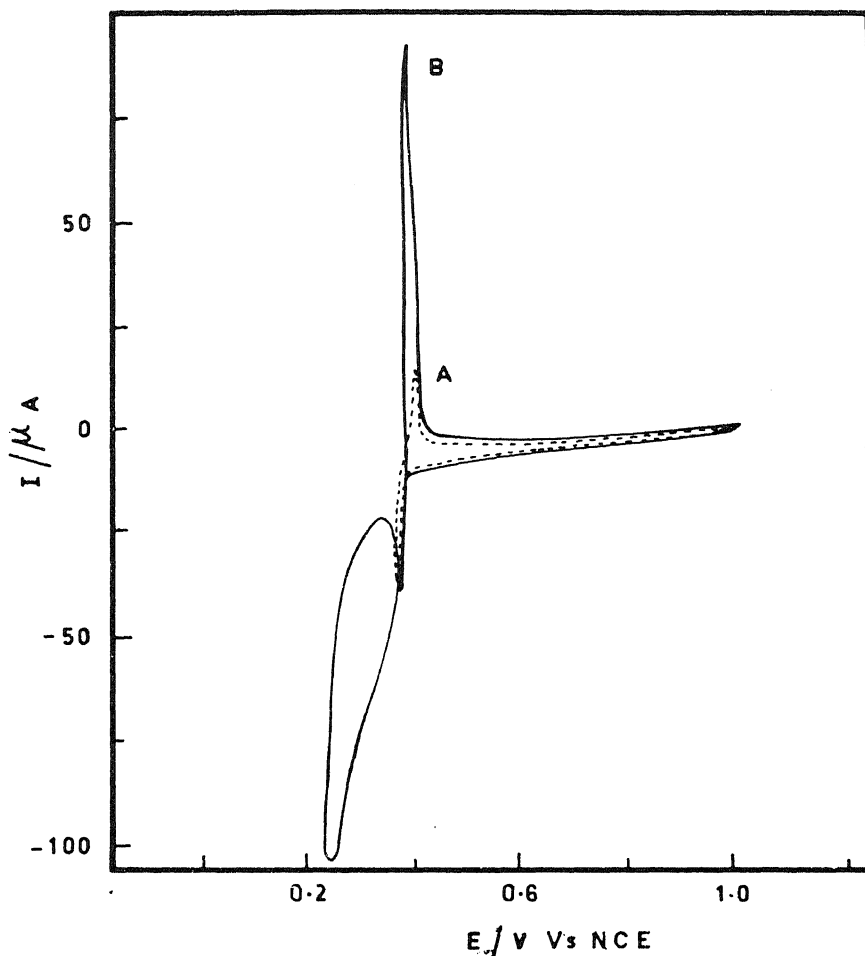


Figure 2. I - E curves obtained by restricting the cathodic potential scan limit to 0.22 V (curve A) and 0.37 V (curve B). The electrolyte was 10^{-2} M mercury(II) nitrate in 0.5 M sulphuric acid, $\nu = 6$ mV/s.

the studies on deposition of metals which led to postulation that the presence of UPD metal resulted in 2-D layer-by-layer growth processes and its absence to 3-D nucleation and subsequent grain growth (Despic 1979; McBreen 1980).

3.3 Characterization of UPD peak

The UPD peak obtained during the deposition of mercury on GCE was further subjected to detailed analysis as follows, to understand the monolayer deposition as due to adsorption or nucleation growth phenomena. This is based on certain diagnostic criteria described to distinguish between the nucleation-growth model from the simple adsorption model for a linear potential sweep input (Bosco and Rangarajan 1981). These diagnostic tests include (i) the value of $\Delta \eta_{1/2}$ on change of sweep rate (ii) I_p vs. E_p^{-1}/E_p^{-2} and (iii) E_p vs. $\ln V$ plots (where I_p and E_p are non-dimensional parameters). The peak width at half height ($\Delta \eta_{1/2}$) was measured

for the UPD peak and was found to vary from 10 to 30 mV on change of sweep rate from 3 to 100 mV/s. If the ECPF of mercury in UPD region occurs by adsorption phenomena, one expects that the $\Delta\eta_{1/2}$ should lie in the range $90/Z$ to $120/Z$ mV, i.e., 45–60 mV for mercury, for Langmuirian adsorption (Schmidt *et al* 1966). Even assuming interactions among neighbouring deposited atoms (i.e. Frumkin type), $\Delta\eta_{1/2}$ is not expected to decrease to such low values as 10 mV (Conway and Gileadi 1962; Bevis and Thomas 1975). On the other hand, the fact that experimentally found $\Delta\eta_{1/2}$ changes from 10 to 30 mV on change of sweep rate from 3 to 100 mV/s, indicates that the monolayer formation follows nucleation-growth model i.e. either progressive or instantaneous (Bosco and Rangarajan 1981a). To further characterize the nucleation-growth processes as progressive or instantaneous, different criteria were checked with the following results. The absence of linearity for both I_p vs. E_p^{-1} (curves A, figure 3) where $I_p = I_p/q_m V$ and $E_p = Vt$ and $\coth E_p$ vs. I_p helped to rule out the possibility of instantaneous nucleation-growth processes. On the other hand, as clear from curve B in figure 3, the plot of I_p vs. E_p^{-2} results in a straight line which suggests the formation of monolayer of mercury by progressive nucleation and growth phenomena. The nucleation parameter (α), calculated from the slope of the curve B in figure 3, corresponds to 542.5. The progressive nucleation growth is further confirmed by the straight line obtained for a plot of E_p vs. $\ln v$ (figure 4). The nucleation-growth rate constant (B_2) was calculated to be $10^{4.34}$ by equating the intercept of the I_p vs. $\ln v$ plot to $1/8 \alpha_c \ln(16 \alpha_c^2) (ZF/4RT)^3/B_2$. The above studies clearly show that the fresh glassy carbon surface is not amenable for deposition of mercury in UPD region. However, subsequent scans result in increasing amounts of deposited

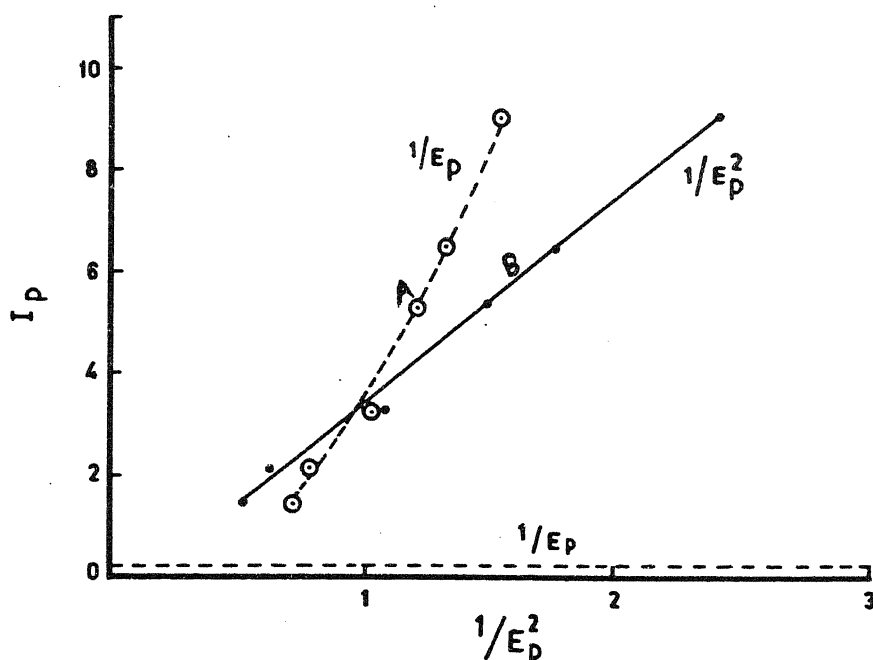


Figure 3. Plot of I_p vs. E_p^{-1} (curve A) and E_p^{-2} (curve B) for UPD of mercury on GCE. I_p , E_p^{-1} and E_p^{-2} are nondimensional quantities.

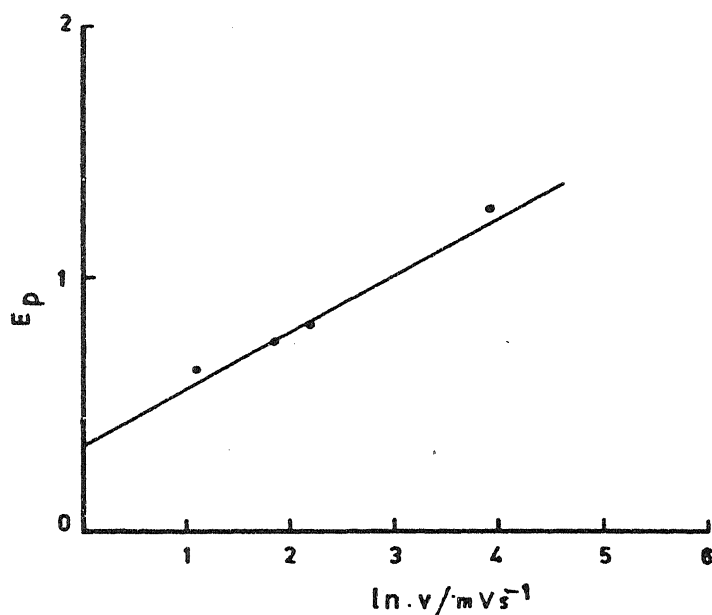


Figure 4. Plot of E_p vs. $\ln v$ for UPD of mercury on GCE where E_p is a nondimensional quantity.

mercury on glassy carbon in the UPD region. The full monolayer of mercury on glassy carbon was achieved only after the 7th scan in spite of the high nucleation parameter and progressive nucleation-growth rate constant. This is probably due to termination of growth of nuclei as the glassy carbon is polycrystalline in nature.

4. Conclusions

The observed increase in the deposition of mercury onto GCE during the first few cycles was traced due to the progressive build-up of monolayers of mercury. The growth of such UPD layers of mercury follows a progressive nucleation-growth mechanism.

List of symbols

a	nucleation parameter in cm/coulomb,
A_0	nucleation rate constant,
B_1, B_2	$g N_0 (\gamma \epsilon k_0)^2 / v^2$, and $g N_0 A_0 (\gamma \epsilon K_0)^2 / v^3$, nucleation-growth rate constants for instantaneous and progressive nucleation, respectively,
E_p	non-dimensional peak potential,
g	lateral interaction parameter,
I_p	non-dimensional peak current,
K_0	growth rate constant,
q_m	monolayer charge,

t	time,
V	$ZFV/4RT$
α_c	cathodic charge transfer coefficient,
γ	molar volume of the new phase,
$\Delta E_{1/2}$	non-dimensional half-peak width,
$\Delta \eta_{1/2}$	peak width at half height,
ε	$1/\eta F$.

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Volume change on mixing: Binary mixtures of isomeric butylamines with chloroform[†]

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Abstract. The excess volume of mixing for 1-aminobutane, 2-aminobutane, 1-amino-2-methylpropane and 2-amino-2-methylpropane with chloroform were determined at 30° by the density method. The V^E were negative for all the systems and showed the following order: 2-amino-2-methylpropane > 2-aminobutane > 1-amino-2-methylpropane > 1-aminobutane. The negative V^E were attributed to complex formation between the amine and chloroform molecules owing to H bonding, while the particular trend was attributed to the decreasing degree of self-association of amine isomers.

Keywords. Excess volume; butylamine; chloroform.

1. Introduction

The behaviour of non-electrolyte solutions of associated liquids is of constant interest. The present work is part of a programme to study the thermodynamic properties of associated liquids (Dutta Choudhary and Mathur 1976; Pradhan and Mathur 1979; Pradhan and Pathak 1983). The V^E for four isomeric butylamines with chloroform has been undertaken in order to obtain the information concerning the structural changes in solution due to hydrogen-bond breaking and making, the effect of branching of alkyl chain on V^E .

2. Experimental

The four isomeric butylamines (S.D. Chemicals, 98% GLC Pure) and chloroform (AR grade, S.D. Chemicals) were further purified by fractional distillation. All the compounds were dried by freshly activated molecular sieves.

The excess volumes of mixing were determined at 30° by the density method, the details of it are reported in an earlier communication (Pradhan 1981). The densities at any composition were reproducible within $\pm 2.0 \times 10^{-5}$ g/ml.

3. Results and discussion

The results on 1-aminobutane (1), 1-amino-2-methylpropane (1), 2-aminobutane (1) and 2-amino-2-methylpropane (1)-chloroform (2) systems have been reported

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Table 1. Volume change on mixing of 1-aminobutane, 1-amino-2-methylpropane, 2-aminobutane and 2-amino-2-methylpropane with chloroform at 30°C.

x_1 mol fraction amine	d_{12} g/ml density of mixture	V^E (ml/mol)
<i>1-Aminobutane (1) + CHCl₃ (2)</i>		
0.0000	1.47143	—
0.0943	1.38771	- 0.075
0.2013	1.29729	- 0.116
0.2981	1.21891	- 0.264
0.4074	1.13400	- 0.348
0.4993	1.06534	- 0.399
0.5494	1.02895	- 0.423
0.6233	0.97432	- 0.429
0.6717	0.94265	- 0.426
0.7524	0.88782	- 0.400
0.8010	0.85544	- 0.359
0.8509	0.82276	- 0.307
0.8984	0.79209	- 0.233
0.9415	0.76472	- 0.156
1.0000	0.72801	—
<i>1-Amino-2-methylpropane (1) + CHCl₃ (2)</i>		
0.0000	1.47044	—
0.1035	1.37779	- 0.130
0.2057	1.29028	- 0.241
0.3147	1.20116	- 0.348
0.3932	1.13952	- 0.417
0.5031	1.05642	- 0.489
0.6069	0.98114	- 0.522
0.6930	0.92090	- 0.517
0.8027	0.84627	- 0.442
0.8497	0.81574	- 0.378
0.9074	0.77836	- 0.269
1.0000	0.71967	—
<i>2-Aminobutane (1) + CHCl₃ (2)</i>		
0.0000	1.46980	—
0.1050	1.37558	- 0.211
0.2041	1.29028	- 0.377
0.3000	1.21099	- 0.504
0.4059	1.12689	- 0.619
0.4971	1.05732	- 0.683
0.6019	0.98044	- 0.718
0.7035	0.90867	- 0.685
0.8047	0.83970	- 0.572
0.9015	0.77585	- 0.358
0.9502	0.74448	- 0.203
1.0000	0.71283	—

Table 1. (contd.)

x_1 mol fraction amine	d_{12} g/ml density of mixture	V^E (ml/mol)
<i>2-Amino-2-methyl propane (1) + CHCl₃ (2)</i>		
0.0000	1.47067	—
0.1035	1.36947	-0.194
0.2099	1.27314	-0.501
0.2972	1.19816	-0.755
0.4044	1.11015	-1.024
0.4548	1.07015	-1.126
0.4998	1.03517	-1.203
0.6060	0.95538	-1.345
0.6591	0.91679	-1.382
0.7257	0.86937	-1.372
0.7831	0.82938	-1.307
0.8255	0.80021	-1.207
0.8822	0.76162	-0.986
0.9492	0.71631	-0.530
1.0000	0.68202	—

in table 1. The maximum uncertainty in V^E values due to the uncertainty of density values, is ± 0.004 ml/mole.

The V^E data have been fitted into the Redlich Kister equation of three parameters, viz.,

$$V^E = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2].$$

The Redlich-Kister parameters along with the standard deviations for these systems have been reported in table 2.

The V^E is negative for these systems and exhibits the following order:

2-amino-2-methylpropane > 2-aminobutane >

($V_{\max}^E = -1.385$ ml/mole) ($V_{\max}^E = -0.718$ ml/mole)

1-amino-2-methylpropane > 1-aminobutane

($V_{\max}^E = -0.525$ ml/mole) ($V_{\max}^E = -0.430$ ml/mole).

The negative V^E is attributed to hydrogen-bonded complex formation in liquid mixtures.

Butylamine isomers are self-associated liquids. So the observed volume change on mixing in these systems is the net effect of a positive volume change due to the breaking of self-associated amine species by chloroform and negative volume change due to hydrogen-bonded complex formation between amine and chloroform molecules. The self-association of butylamine isomers decrease according to the order:

1-aminobutane > 1-amino-2-methylpropane > 2-aminobutane >
2-amino-2-methylpropane.

Table 2. Redlich-Kister parameters for volume change on mixing of isomeric butylamines-chloroform systems at 30°C.

System	B ml/mole	C ml/mole	D ml/mole	Standard deviation
1-Aminobutane + CHCl ₃	-1.5591	-1.1182	-0.2207	0.015
1-Amino-2-methyl- propane + CHCl ₃	-1.9332	-1.0715	-0.5192	0.006
2-Aminobutane + CHCl ₃	-2.7391	-1.1117	-0.6436	0.002
2-Amino-2-methyl- propane + CHCl ₃	-4.7359	-4.4858	-2.1624	0.045

The contribution of the positive volume change due to the dissociation of polymeric amine species decreases accordingly, which explains the observed trend of V^E in the systems presently studied.

From the molar volumes of these butylamines, the negative V^E due to accommodation of chloroform molecules in the liquid structure of amines is also expected to increase in the same observed manner. However, its contribution is expected to be small.

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A multistage adsorption process in 15-15' *cis* β -carotene crystal: Electrical conductivity enhancement on chemical vapour adsorption

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Abstract. The phenomenon of conductivity enhancement on adsorption of various chemical vapours has been used as a probe to study the adsorption and desorption process in 15-15' *cis*- β -carotene crystals. The kinetics follow a modified Roginsky-Zeldovich equation. From the analyses of the kinetics, the adsorption has been found to be multistage at higher vapour pressure. An additional physisorption stage shows up in the initial stage of the well-known three stage adsorption process. Measures of activation energies of adsorption and desorption at different stages have been estimated.

Keywords. Multistage adsorption process; β -carotene crystal; electrical conductivity enhancement; chemical vapour adsorption; modified Roginsky-Zeldovich equation.

1. Introduction

On adsorption of various chemical vapours and gases, the electrical conductivity of organic-semiconductors changes appreciably. Using this property as a probe, we have studied the adsorption and desorption processes in some polyene crystals (Ghosh *et al* 1980; Mitra *et al* 1985; Sircar *et al* 1983). Generally in polyene crystal-vapour systems a simple two-stage adsorption process has been found to be operative (Ghosh *et al* 1980; Sircar *et al* 1983), but in case of lycopene (Mitra *et al* 1985), as well as in some nitro-aromatic crystals (Ghosh *et al* 1981), a three-stage adsorption process has been identified. In a two-stage process, the first stage gives a Lennard-Jones potential energy curve, followed by a second-stage where a transition over a potential barrier to a potential well occurs. In a three-stage process, there is an additional stage in which a deeper potential well is reached by activation over a second barrier, and strongly bound complexes between the vapour molecules and the surface molecules of the crystals are formed. In order to examine if there are adsorption processes where additional stages are involved, we have extended our investigation to a large number of polyene crystal-vapour systems. In 15-15' *cis*- β -carotene crystals we have observed a multistage adsorption process which is reported in this paper. We also report the activation energies of adsorption and desorption in different stages as estimated by kinetic data analyses using a modified Roginsky-Zeldovich equation.

2. Experimental

Highly purified 15-15' *cis*- β -carotene, obtained as a gift from Hoffmann La Roche and Co. Ltd., Switzerland, was used without any further purification. We have

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used the sandwich cell technique with a conducting glass and a stainless steel electrode. Spectrograde quality (E Merck/BDH) reagent chemicals, ethyl acetate, ethanol and methanol were used. To introduce various vapours into the chamber, nitrogen gas, used as the carrier, was passed at a constant rate of flow to maintain a particular vapour pressure through a bubbler containing the solvent kept at the desired temperature. The sample cell was kept at room temperature (≈ 300 K). Repeated heat cycling of the sample initially in vacuum and finally in a dry nitrogen atmosphere ensured desorption of water vapour or any other adsorbed gases. The experimental details has been described earlier (Mallik *et al* 1979).

3. Results and discussion

3.1 The effect of adsorption of vapours on dark conduction

The change in the dark current in a 15-15' *cis*- β -carotene powder cell, kept at a fixed temperature (300 K), upon adsorption and desorption of ethanol vapour at different partial pressures is shown in figure 1. At the lowest pressure (35 mm), as the powder sample adsorbs the vapour from the chamber atmosphere, the current increases and tends to reach a saturation value. This behaviour is similar to that observed in case of lycopene and other polyene crystals (Mitra *et al* 1985; Sircar *et al* 1983). But at higher pressures, with the adsorption of vapour the current increases but passes through a hump before it reaches the saturation value. Here a pseudo-equilibrium is reached wherefrom the current briefly decreases but increases again and finally reaches the real saturation value. The adsorption process in 15-15' *cis*- β -carotene is, however, slow compared to that in other polyenes where saturation value is reached in 15–20 min (Ghosh *et al* 1980; Mallick *et al* 1979). The maximum value of current reached at equilibrium, under a particular set of experimental conditions, depends on the vapour pressure of the reagent chemical and the temperature of the sample cell. When the chamber is flushed with dry nitrogen gas the vapour is desorbed from the crystal surface and the current decreases but does not come back exactly to the original value, suggesting that both physisorption and chemisorption of vapours occur. Dry nitrogen gas flow in the ambient atmosphere is carefully regulated so that the partial pressure of the gas mixture is kept below the saturation limit and that no readsorption takes place. Similar adsorption and desorption curves are obtained with ethyl acetate and methanol also.

3.2. Dependence of the dark conductivity on the ambient vapour pressure

We have obtained an exponential dependence of the conductivity on the vapour pressure of the reagent chemical. This is similar to our previous observation in the case of naphthyl polyenes (Sircar *et al* 1983) and lycopene (Mitra *et al* 1985).

For adsorption of a small amount of vapour molecules, the conductivity $\sigma_A(m)$ follows the relation (Misra *et al* 1968),

$$\sigma_A(m) = \sigma_V \exp(\alpha m), \quad (1)$$

where σ_V is the conductivity before adsorption, α is a constant for a specific semiconductor-vapour system and m is the amount of vapour adsorbed; m depends

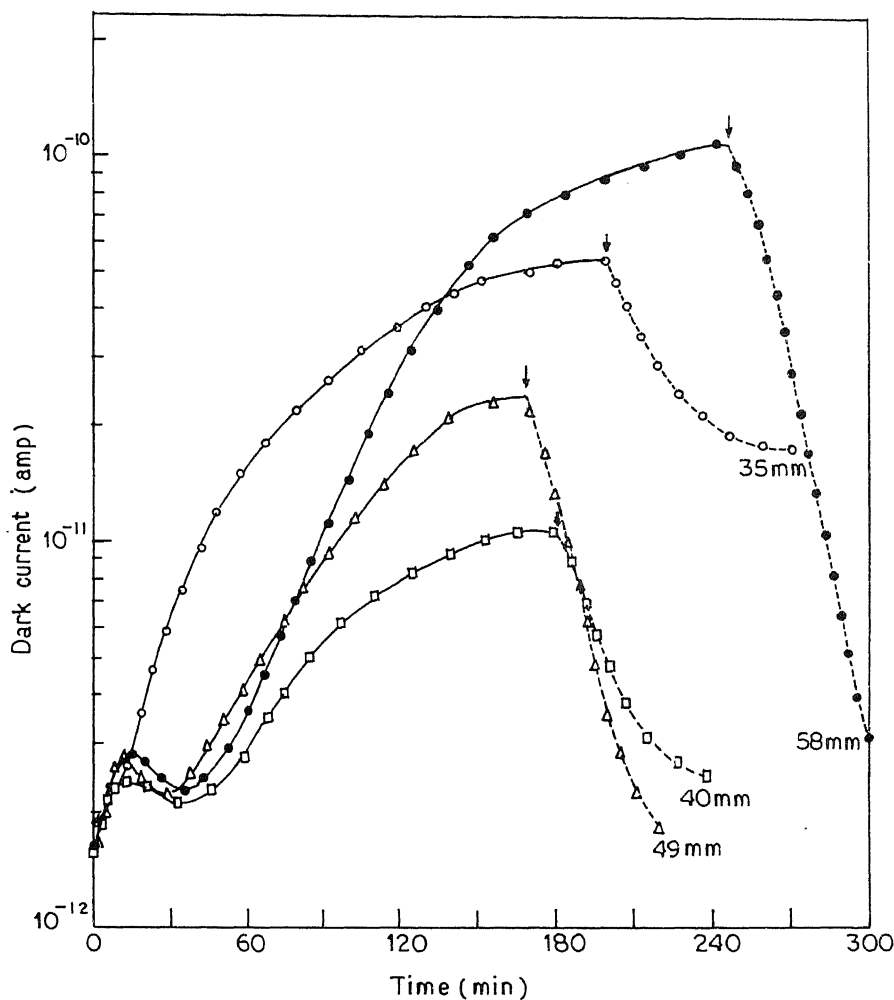


Figure 1. The change in dark current in a 15-15' *cis* β -carotene powder cell, kept at 300 K, on adsorption and desorption of ethanol vapour at different vapour pressures. The arrows indicate the initiation of desorption. Solid lines are for adsorption and broken lines for desorption.

on the partial pressure p of the reagent chemical and also on time of exposure (before saturation is reached). Thus in the short time domain,

$$m(t) = Q(t) \cdot p, \quad (2)$$

where $Q(t)$ is a function of time. At equilibrium when saturation is reached,

$$m_0 = Q_0 \cdot p,$$

and Q_0 now becomes independent of time. When a small fraction of surface is covered by gas molecules, (2) is expected from the Langmuir adsorption isotherm.

At equilibrium,

$$\sigma_A(m_0) = \sigma_V \exp(\alpha \cdot Q_0 \cdot p) \quad (3)$$

A plot of $\log \sigma_A(m_0)$ vs. p is expected to be linear. Our experimental results are in good agreement as shown in figure 2. To obtain $\sigma_A(m_0)$, we have extrapolated the $\log \sigma_A$ vs. t curves (figure 1) over longer time periods. Also only the adsorption curves with humps in the short time region have been plotted as these represent similar adsorption process.

3.3 Adsorption and desorption kinetics

From a modified Roginsky-Zeldovich equation for adsorption and desorption kinetics, one can derive, for time dependence of dark conductivity during adsorption and desorption processes, the expressions,

$$\log \sigma_A = (\alpha KT/\beta) \log(t+t_0) + \text{constant}, \quad (4)$$

for adsorption, and

$$\log \sigma_A^* = (\alpha KT/\beta^*) \log(t+t_0^*) + \text{constant}, \quad (5)$$

for desorption.

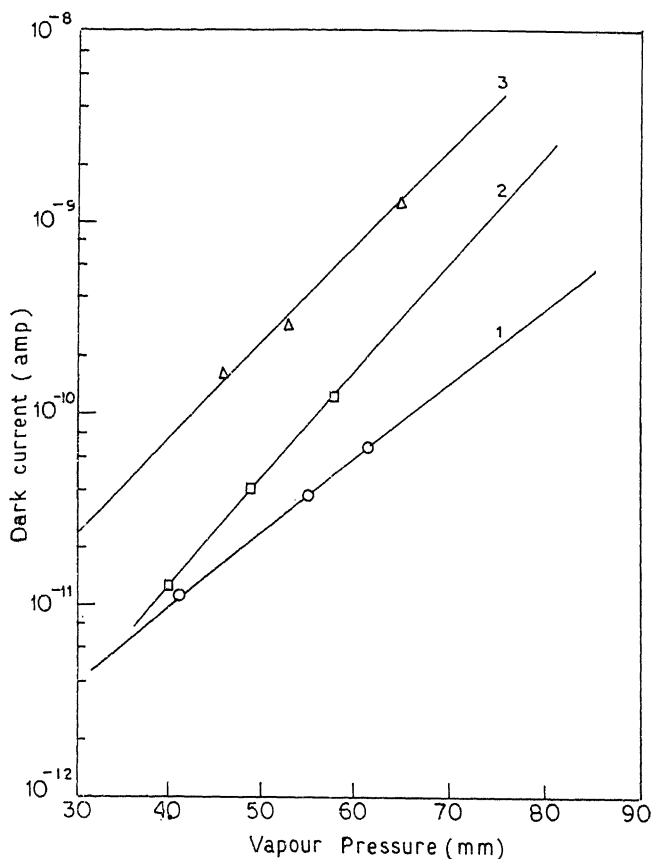


Figure 2. Semilog plot of dark current enhancement on adsorption as a function of vapour pressure of various reagent chemicals in 15-15' *cis* β -carotene powder cell kept at 300 K. The straight lines 1, 2 and 3 are for methanol, ethanol and ethyl acetate, respectively.

Here α is a constant for a crystal-vapour pair and is a measure of the strength of interaction between the vapour molecule and the crystal, β and β^* are measures of activation energies of adsorption and desorption, respectively, k is the Boltzmann constant and T is the absolute temperature.

Choosing t_0 and t_0^* empirically, linear plots of $\log \sigma_A$ vs. $\log (t+t_0)$ and $\log \sigma_A^*$ vs. $\log (t+t_0^*)$, as expected, are generally obtained for various chemical vapour adsorption (and desorption) on polyene crystals (Ghosh *et al* 1980; Sircar *et al* 1983; Mallik *et al* 1979).

Such plots for adsorption and desorption of ethanol and methanol vapours on 15-15' *cis*- β -carotene are shown in figures 3 and 4, respectively. The time indicated in the abscissa is measured from the initiation of the adsorption (or desorption) and linear plots are obtained, but the behaviour is different from that observed with other polyene crystals (Mitra *et al* 1985; Sircar *et al* 1983). In other polyenes only

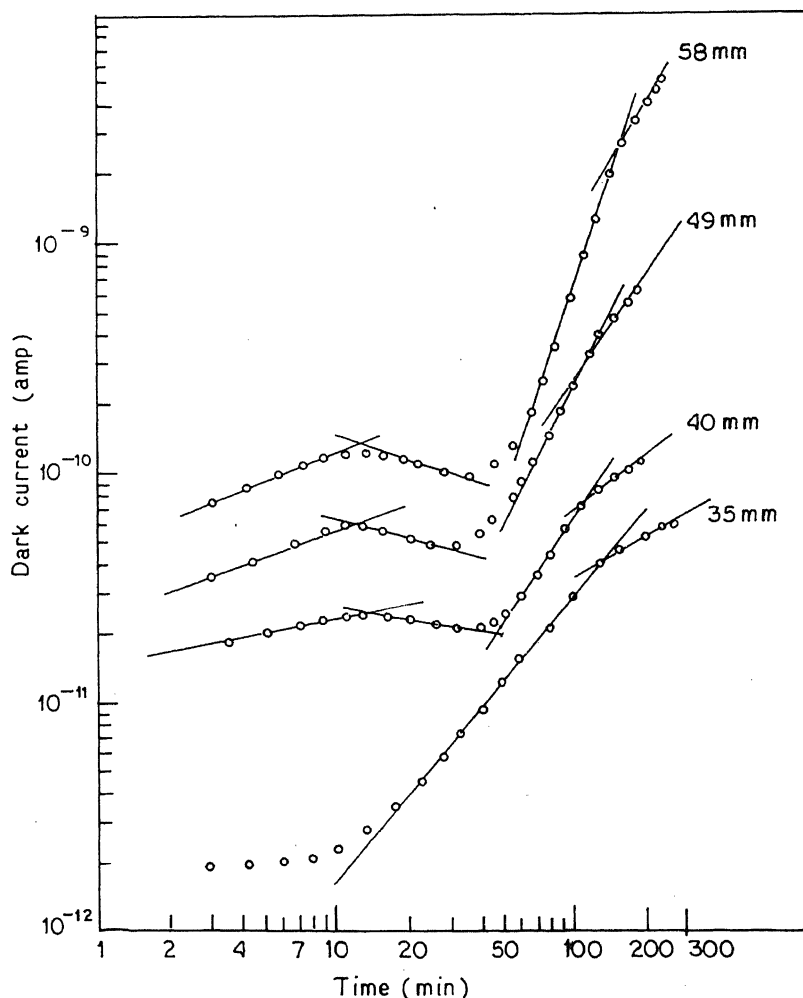


Figure 3. Kinetic data for ethanol vapour adsorption on 15-15' *cis* β -carotene crystals plotted according to the modified Roginsky-Zeldovich [equation (8)].

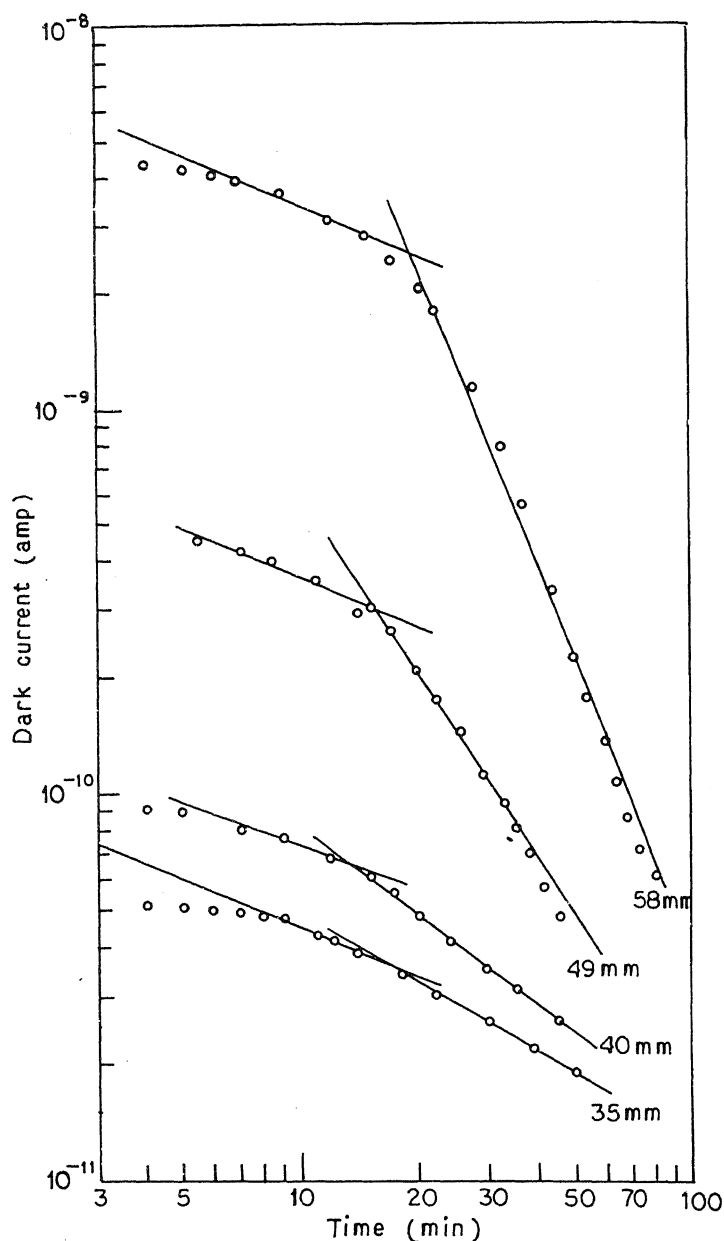


Figure 4. Kinetic data for ethanol vapour desorption from 15-15' *cis* β -carotene crystals plotted according to (9).

one or two line segments are obtained in the time region before saturation is reached and on reaching saturation there is no further enhancement of conductivity and the second or third segment of the straight line shows zero slope. But in the present case of 15-15' *cis*- β -carotene we get another additional straight line segment at the short time region in addition to the two straight lines in the longer time regions. This suggests a third activation in the adsorption process. The

modified Roginsky-Zeldovich equation having three activation energies for adsorption and desorption in different time domains now becomes

$$\frac{dm}{dt} = A \exp\left(-\frac{\beta_1 m}{KT}\right) \exp\left(-\frac{\beta_2 m}{KT}\right) \exp\left(-\frac{\beta_3 m}{KT}\right), \quad (6)$$

$$-\frac{dm}{dt} = A^* \exp\left(-\frac{\beta_1^* m}{KT}\right) \exp\left(-\frac{\beta_2^* m}{KT}\right) \exp\left(-\frac{\beta_3^* m}{KT}\right), \quad (7)$$

and assuming that multistage activation processes are operative in different time regions, (4) and (5) in the modified forms are

$$\begin{aligned} \log \sigma_A = & \frac{\alpha KT}{\beta_1} \log(t + t_0) + \frac{\alpha KT}{\beta_2} \log(t + t_0) \\ & + \frac{\alpha KT}{\beta_3} \log(t + t_0) + \dots + \text{constant}, \end{aligned} \quad (8)$$

for adsorption, and

$$\begin{aligned} \log \sigma_A^* = & \frac{\alpha KT}{\beta_1^*} \log(t + t_0^*) + \frac{\alpha KT}{\beta_2^*} \log(t + t_0^*) \\ & + \frac{\alpha KT}{\beta_3^*} \log(t + t_0^*) + \dots + \text{constant}, \end{aligned} \quad (9)$$

for desorption.

The three terms dominate the three time domain of adsorption and desorption kinetics. We have obtained the values of

$$\begin{aligned} \beta_1' \left(= \frac{\beta_1}{\alpha} \right), \quad \beta_2' \left(= \frac{\beta_2}{\alpha} \right), \quad \beta_3' \left(= \frac{\beta_3}{\alpha} \right), \\ \beta_1^{*'} \left(= \frac{\beta_1^*}{\alpha} \right), \quad \beta_2^{*'} \left(= \frac{\beta_2^*}{\alpha} \right), \quad \beta_3^{*'} \left(= \frac{\beta_3^*}{\alpha} \right), \end{aligned}$$

at different vapour pressures from the slopes of $\log \alpha_A$ vs. $\log t$ plots. These are presented in table 1. All β' show strong pressure dependence, whereas $\beta_1^{*'}$ and $\beta_3^{*'}$ are weakly pressure dependent, $\beta_2^{*'}$, however, is pressure independent.

For adsorption of various chemical vapours on lycopene crystals, we observed a three-stage adsorption process, the second stage of which represents a weakly-bound complex and the third stage a strongly bound complex where the vapour molecules are activated into a deep potential well. In the present case, for higher pressures of the vapour, an additional stage of physisorption is observed in the short time region. This shows up as a hump in the adsorption curve. The low value of energy difference between the two potential energy minima in the second stage suggests that the crystal-vapour system at these stages could be in dynamic equilibrium and some molecules may be desorbed from the second potential well. The other stages are similar to that observed in case of adsorption on lycopene

Table 1. Vapour pressure dependence of the factors β^{*} and β^{**} for adsorption and desorption kinetics, respectively, on adsorption of different vapour.

Reagent chemical	Vapour pressure (mm)	β_1' (eV) ($\times 10^{-2}$)	β_2' (eV) ($\times 10^{-2}$)	β_3' (eV) ($\times 10^{-2}$)	β_1^{*} (eV) ($\times 10^{-2}$)	β_2^{*} (eV) ($\times 10^{-2}$)	β_3^{*} (eV) ($\times 10^{-2}$)
Ethanol	35	—	2.03	4.49	—	5.88	4.74
	40	12.5	1.64	3.06	13.00	6.52	3.22
	49	6.58	1.14	1.63	7.40	5.93	1.7
	58	5.68	0.76	0.90	6.40	5.69	1.04
Methanol	35	—	3.40	4.30	—	7.03	6.01
	41	—	1.53	2.70	—	6.98	2.82
	55	8.77	0.66	1.93	11.00	6.25	1.95
	61.5	7.33	0.56	1.27	8.4	6.47	1.87
Ethyl acetate	39	—	1.13	2.02	—	3.27	2.03
	46	8.07	1.06	1.80	—	3.16	1.82
	53	6.41	0.98	1.52	7.10	3.24	1.62
	65	5.68	0.91	1.43	6.10	3.12	1.52

crystals. A model diagram for this adsorption process is shown in figure 5. A large value of β_2^{*} , the desorption activation energy, suggests a strongly bound complex formation in the final stage. The pressure independence of β_2^{*} is understandable, since such complexes are like chemical species and β_2^{*} is a measure of the binding energy of the complex. Evaluation of true binding energy is not possible in our experiment as we cannot measure the interaction energy between the vapour molecule and the crystal, the amount of vapour adsorbed and the entropy factor of the system. Our results however, confirm a multistage adsorption process in the 15-15' *cis* β -carotene crystal-chemical vapour system.

3.4 Type of interaction between the adsorbed vapour and the semi-conducting material

The nature of the bonding of the surface molecules of the semi-conducting crystals with the adsorbed vapour molecules is of interest as it is expected to elucidate the conductivity enhancement mechanism on vapour adsorption. In physisorption, the binding energy between the molecules is very small (a few kcal/mol) and is thought to be due to van der Waal complex formation. Chemisorption, on the other hand, may have binding energy values over a wide range and may involve various types of charge transfer complex formation, hydrogen-bonding and also new chemical species formation. Besides, many other subtle interactions involving dipole-dipole, ion-dipole and dielectric factors are possible.

In our adsorption kinetic plot (figure 1) the hump in the short time region represents a state of dynamic equilibrium between the first and the second stage of the proposed adsorption model (figure 5). This possibly is due to weak van der Waal complex formation. Charge transfer (CT) complex formation has been widely held responsible for current enhancement on gas adsorption in semiconductors (Labes and Rudyj 1963; Reucroft *et al* 1963, 1962). As polyenes are known to act both as electron donors and electron acceptors (Platt 1959; Pullman and Pullman

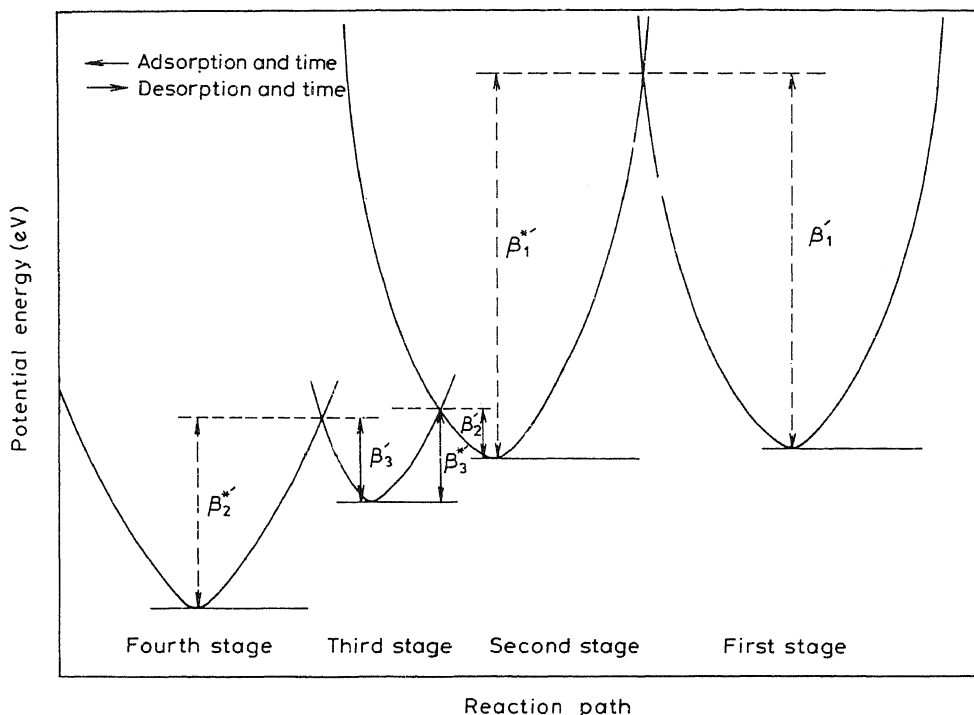


Figure 5. Potential energy curves for multistage vapour adsorption in 15-15' *cis* β -carotene semiconductor explaining the three-region linearity in modified Roginsky-Zeldovich plots. β_1' , β_2' and β_3' are, respectively, the first, second and third-stage activation energy measures of adsorption, and β_1'' , β_2'' and β_3'' are the activation energy measures of desorption for the second, third and fourth-stages, respectively.

1963). Formation of CT complexes between *cis*- β -carotene and the adsorbed molecules is possible. CT complexes may be of different types. In contact CT complexes, donors and acceptors come in contact with each other momentarily and charge transfer takes place (Slifkin and Allison 1967). Interaction energy of such contact CT is small and is of the same order as in van der Waal interaction (Matsuo and Higuchi 1968). Stable CT complexes have higher binding energy. CT interaction depends on the ionisation potential of the donor (I_D) and the electron affinity of the acceptor. In table 2, we show the I_D of the vapours used and the conductivity enhancement on their adsorption. They are found to be in inverse order (i.e. in the order of electron affinities) for adsorption at low vapour pressure where the initial physisorption stage is absent. At higher pressures, conductivity enhancement for ethyl acetate adsorption is significantly low. Hydrogen-bond formation is unlikely in the present case as ethyl acetate cannot form such bonds with *cis*- β -carotene (though alcohols can). We also discard the possibility of the formation of new chemical species as heat cycling of the sample in vacuum ensures complete desorption of the vapour. We, therefore, believe that the third and fourth stages of adsorption represent weakly and strongly bound CT complexes, respectively.

During exposure of the polycrystalline powder sample to the vapours, the vapour molecules may occupy the interspace between the crystallites and form a dielectric medium different from the original one. If the conductivity change on adsorption of

Table 2. Rise in the dark current in 15–15' *cis* β -carotene powder cells at 300 K due to adsorption of various vapours at 35 and 58 mm pressures.

Vapour	Dielectric constant at 25°C	Ionisation potential (eV)	σ_A/σ_V	
			35 mm	58 mm
Ethyl acetate	6.00	10.11	63	36
Ethanol	24.30	10.50	32	75
Methanol	32.60	10.85	12	24

vapours is due to such physical mixing, a relationship between the conductivity enhancement and dielectric constant of the vapours used is expected. The static dielectric constant (Treiber and Koren 1951) of the vapours used are, as shown in table 2, not in the same order of semiconduction current enhancement at the low vapour pressure. Further work on more semiconductor-vapour systems is required before any conclusion can be drawn about the nature of the bond formation at different stages of adsorption and also the role of the dielectric constant change in conductivity enhancement.

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A new *B-Z* oscillatory reaction with mixed organic substrates

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Abstract. Reaction systems, viz., (i) $\text{KBrO}_3/\text{Mn(II)}$ /organic substrate/ H_2SO_4 and (ii) KBrO_3 /ferroin/organic substrate/ H_2SO_4 (where organic substrate = glycollic or mucic acid) could not exhibit chemical oscillations. However, *B-Z* chemical waves have been recorded under novel conditions by taking mixtures of centimolar glycollic acid and millimolar mucic acid as organic substrate in the presence of mixtures of Mn(II) and ferroin as catalyst. The use of teflon beakers as reaction vessels for the reproducibility of chemical waves is a new feature of this study.

Keywords. Oscillatory reaction; chemical oscillation; mixed organic substrates; teflon beaker.

1. Introduction

The study of chemical oscillations has emerged as an increasingly important field to chemists and biochemists in recent years and provides an efficient tool for understanding the mechanisms of a variety of organic, inorganic and biochemical reactions (Nicolis and Portnow 1973; Field and Noyes 1974; Degn 1972; Edelson 1975). Although there are some reports on *B-Z* oscillators derived from phenols, amines and dicarboxylic acids possessing a hydroxy moiety and active methylene groups (Nitzun *et al* 1974; Rastogi *et al* 1978; Ganapathisubramanian *et al* 1978; Ramanathan and Ramaswamy 1983), not much work appears to have been done on the oscillatory systems containing glycollic (GA) and mucic acid (MA) as substrates. Our preliminary studies indicate that oscillations are initiated only under specific conditions, viz., (i) when a mixture of metal ions [Mn(II) + ferroin] is used as a catalyst; (ii) when a mixture of organic compounds (centimolar GA + millimolar MA) is employed as substrate. This prompted us to communicate the salient features of the present study in order to gain an insight into the synergistic activity of mixed catalysts and the characteristics of chemical waves. The use of 'teflon' beakers as reaction vessels for the reproducibility of waves is also a new feature of this study.

2. Experimental

Glycollic acid, mucic acid, MnSO_4 and KBrO_3 are Fluka reagents. A $0.025 \text{ mol dm}^{-3}$ ferroin solution has been procured from Riedel-de Haen (AG), Hannover. The other reagents are E Merck (GR) samples. Requisite amounts of various reagents are mixed in a "teflon" beaker and the reaction is initiated by the

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addition of KBrO_3 . The temporal EMF oscillations have been recorded on a Systronics-Digital potentiometer (Model-335) comprising a bright platinum indicator electrode and saturated calomel electrode system connected through a KNO_3 bridge to a Systronics-Strip chart recorder (model-1501). Electromagnetic stirring of the reaction mixture ensured homogeneity of the solution. Oscillations could not be traced out either in a glass or a polythene beaker when relatively low concentrations of mixtures of GA and MA (centimolar GA + millimolar MA) were used as organic substrate. However, this problem has been overcome by using teflon beakers as reaction vessels. A high degree of reproducibility has been observed by repeating the same experiment at least half-a-dozen times in teflon beakers (figure 1). Further, the evaporation of thin surface films formed on the walls of polythene beakers takes a much longer time, while it takes only a couple of minutes in the case of teflon beakers. The potentiometric traces thus observed have been utilised to evaluate the characteristic properties of chemical waves, viz., time of initiation (T_i), time period (T_p), life time of oscillations (T_l) and total number of oscillations (n) etc. At any particular temperature the amplitude of the wave generally lies in the range 150 to 200 mV in the initial stages but decreases with time.

3. Results and discussion

The *B-Z* reagent alone could not generate chemical waves in the experimental concentration ranges of the various reactants mentioned in table 1 in H_2SO_4 media.

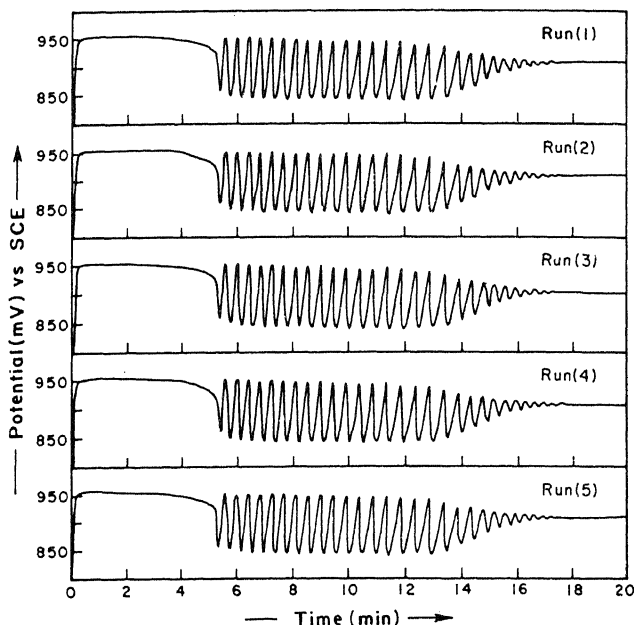


Figure 1. Runs 1 to 5 (reproducibility of waves): plots of potential (mv) vs. time (min) in glycolic acid system. $[\text{KBrO}_3] = 0.06 \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4] = 1.07 \text{ mol dm}^{-3}$; $[\text{GA}] = 0.100 \text{ mol dm}^{-3}$; $[\text{Mn(II)}] = 0.004 \text{ mol dm}^{-3}$; $[\text{Ferroin}] = 4.00 \times 10^{-5} \text{ mol dm}^{-3}$; temperature = 300 K.

Neither Mn(II) (10^{-4} to 10^{-2} mol dm $^{-3}$) nor ferroin (10^{-5} to 10^{-3} mol dm $^{-3}$) alone could catalyse the process and initiate oscillations. It is also interesting to note that the potentiometric traces are absent when any one of the components, viz., Mn(II), ferroin, GA or mucic acid (MA) are absent in the system with $[GA] < 0.05$ mol dm $^{-3}$. When $[GA] > 0.05$ mol dm $^{-3}$, chemical waves have been recorded even in the absence of mucic acid. However, the presence of Mn(II) and ferroin is an essential factor. Further, periodic waves have been noticed only when teflon beakers are used as reaction vessels at low concentration ranges of GA. All efforts are unsuccessful when a glass beaker or polythene beaker is used as reaction vessel.

3.1 Salient features of the study in mixed organic substrate system

Potential versus time curves of the study show that the amplitude (A) of the chemical waves decreases, while the time period (T_p) increases with time (figure 2). T_i versus $[KBrO_3]$ plots show a maximum in the curve with an increase in the concentration of bromate (0.015 to 0.06 mol dm $^{-3}$, table 1). However, the plots of (a) T_p versus $[KBrO_3]$, (b) T_i versus $[KBrO_3]$, and (c) n versus $[KBrO_3]$, show a minimum in the curve. An increase in $[H_2SO_4]$ shows a linear decrease in T_i , T_p , T_l , while the number of oscillations remain almost unaffected. A variation in $[Mn(II)]$ (0.004 to 0.02 mol dm $^{-3}$) shows that T_i , T_p and the number of oscillations decrease with an increase in $[Mn(II)]$. A large variation in $[ferroin]$ shows that T_i increases with an increase in $[ferroin]$ while the other characteristics of chemical waves show an irregular trend. Surprisingly, the number of oscillations also do not show a linear dependence on $[ferroin]$. Owing to the low solubility of mucic acid in water, experiments could not be tried with higher concentrations. However, the variation from 0.001 to 0.004 mol dm $^{-3}$ could not initiate oscillations at all, while a two-fold increase of $[MA]$ from 0.005 to 0.01 mol dm $^{-3}$ shows that T_i , T_p and n are slightly increased, while T_l is independent of $[MA]$. With an increase in $[GA]$, T_i ,

Table 1. Characteristics of chemical waves as a function on [reactant] in mixed organic substrate (GA + MA) system at 300 K.

$10^2 [KBrO_3]$	$[H_2SO_4]$	$10^2 [Mn(II)]$	$10^5 [ferroin]$	$[GA]$	$10^3 [MA]$	T_i	T_p	T_l	
(mol dm $^{-3}$)		(mol dm $^{-3}$)		(mol dm $^{-3}$)		(minutes)			(n)
1.50	2.136	1.10	4.00	0.050	5.00	5.00	1.75	7.10	4
3.00	2.136	1.00	4.00	0.050	5.00	5.60	1.17	3.50	3
6.00	2.136	1.00	4.00	0.050	5.00	2.20	1.90	9.30	5
3.00	4.272	1.00	4.00	0.050	1.08	0.208	0.208	0.416	2
3.00	0.534	1.00	4.00	0.050	5.00	22.6	14.7	44.3	3
3.00	2.136	1.00	4.00	0.100	5.00	2.50	0.48	4.5	8
3.00	2.136	1.00	4.00	0.200	5.00	0.90	0.22	2.3	11
3.00	2.136	1.00	4.00	0.100	10.00	2.50	0.56	6.0	10
3.00	2.136	2.00	4.00	0.100	5.00	3.30	0.80	2.4	3
3.00	2.136	0.40	4.00	0.100	5.00	1.90	0.20	4.1	22
3.00	2.136	0.40	1.00	0.100	5.00	1.00	0.35	0.70	2
3.00	2.136	0.40	2.00	0.100	5.00	1.15	0.14	2.10	19
3.00	2.136	0.40	4.00	0.200	5.00	1.40	0.04	1.40	28
3.00	2.136	0.40	10.00	0.100	5.00	4.33	0.22	1.30	6

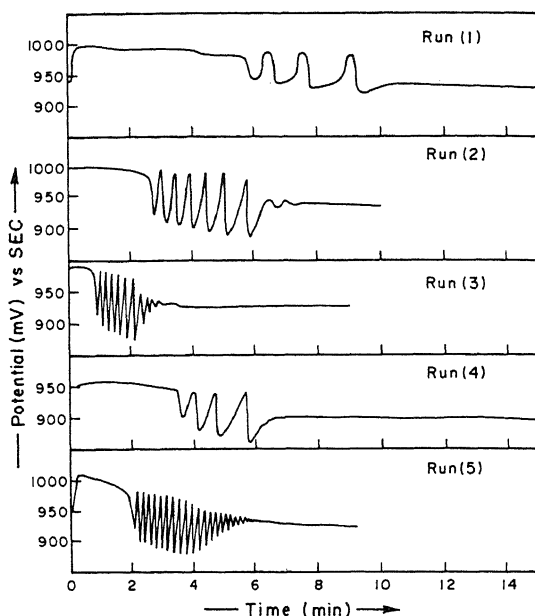


Figure 2. Effect of [reactant] in mixed organic substrates: plots of potential (mV) vs. time (min) in mixed organic substrates at 300 K.

Run 1 $[\text{KBrO}_3] = 0.030 \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4] = 2.14 \text{ mol dm}^{-3}$; $[\text{Mn(II)}] = 0.010 \text{ mol dm}^{-3}$; $[\text{Ferrioin}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{MA}] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{GA}] = 0.050 \text{ mol dm}^{-3}$; Run 2 $[\text{KBrO}_3] = 0.030 \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4] = 2.14 \text{ mol dm}^{-3}$; $[\text{Mn(II)}] = 0.010 \text{ mol dm}^{-3}$; $[\text{Ferrioin}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{GA}] = 0.10 \text{ mol dm}^{-3}$; $[\text{MA}] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$; Run 3 $[\text{GA}] = 0.200 \text{ mol dm}^{-3}$, other conditions as in run 1; Run 4 $[\text{Mn(II)}] = 0.020 \text{ mol dm}^{-3}$, other conditions as in run 2; Run 5 $[\text{Mn(II)}] = 0.004 \text{ mol dm}^{-3}$, other conditions as in run 2.

T_p and T_l decreased while the number of oscillations increased. Owing to the irregular trend of the dependence of oscillations on [reactants], analytical equations which could fit the data could not be attempted. However, some mechanistic points can be highlighted with the available data and the other observations during the course of the experiment. Immediately after the addition of KBrO_3 to each set, the pink colour of the solution instantaneously changed to bluish green which indicates the formation of a ferrin complex showing a band at 610 nm. Sufficient time was available to test this prior to the start of the oscillations. Once the oscillations are initiated, the bluish green colour changed to a cherry brown colour indicating the formation of Mn(III) which shows a band around 500 nm in the visible region. Once the oscillations are initiated, the colour of the solution periodically changes from cherry brown to yellow indicating the formation of Br_2 . A stable yellow colouration is observed after the completion of oscillation. When kept overnight the solution became completely colourless. The role of mucic acid may be attributed to the formation of a metal chelate either with Mn(II) and/or Fe(II) because it is a polydentate ligand with six coordinate sites. However, the possibility of coordination to Fe(II) can be ruled out because Fe(II) is already in the form of

ferroin [Fe(II)-phenanthroline complex]. Further, it is interesting to note that, the oscillatory behaviour is more pronounced under conditions of relatively low [Mn(II)] ($0.004 \text{ mol dm}^{-3}$) and [MA] ($0.005 \text{ mol dm}^{-3}$). This trend can be readily seen from table 1 which shows that (n) the number of oscillations are maximum ($= 28$), though the life time is relatively low, time of initiation is moderate, and T_p is very low. It is, therefore, not unreasonable to visualise the oxidation of ferroin by BrO_3^- as the initial step to give ferrin which subsequently reacts with the [M(II)-MA] adduct. Once sufficient amounts of ferrin/ferroin and/or [Mn(III)-MA]/[M(II)-MA] result, oscillations are observed. As in the case of other B-Z oscillators, in this study also glycollic acid reacts with Br_2 during the course of the reaction. Addition of olefinic monomers such as acryl amide and acrylo nitrile etc. inhibited the oscillations thus indicating the formation of free radicals during oscillations. An increase in temperature decreases the amplitude of the chemical wave significantly though the number of oscillations remained almost unaffected. The other oscillation properties, viz., T_i , T_p and T_l are also decreased remarkably with an increase in temperature. Although glycollic acid forms a bromo derivative during the course of reaction, the end products have been analysed as CO_2 and formaldehyde (Feigl 1966; Vogel 1967). In our earlier paper we have reported that oxidation of glycollic acid by Mn(III) yields formaldehyde as the end product (Rajanna *et al* 1980). By a perusal of the salient features of the oscillations, coupled with the foregoing discussion, a plausible mechanism to explain the characteristics of the oscillations can be given, with the oxidation of ferroin to ferrin as the first step. Ferrin, being a better oxidant than Fe(III) and/or KBrO_3 , may further oxidise the [Mn(II)-MA] adduct to give a [Mn(III)-MA] adduct. The chelate thus formed in turn reacts with Br^- to form molecular bromine. Bromine may then react with glycollic acid to yield the bromoderivative and Br^- and thus complete the cycle. A repetition of these steps may produce oscillations.

3.2 Salient features of Mn(II) + ferroin catalysed chemical waves of glycollic acid system

By and large the behaviour of chemical waves is clear and follows a regular pattern in this part of the study. Properties of oscillations generally exhibit either a linear increase or decrease with [reactants] (figure 3). The log-log plots of oscillation parameter as a function of [reactant] are linear with specific values of slope and intercepts. From the slope and intercept values, analytical expressions which can fit into the observed data have been proposed and compiled in table 2. The mechanistic features are by and large similar to those discussed in the preceding section. Immediately after the addition of KBrO_3 the colour of the solution turned into greenish blue indicating the formation of ferrin. Ferrin thus formed oxidises Mn(II) to Mn(III). The manganic ion may further oxidise Br^- to molecular bromine. Glycollic acid takes up the bromine to form a bromo glycollic acid moiety and Br^- , and thus completes one cycle. By and large a substantial decrease in the time of initiation (T_i), life time (T_l) and time period (T_p) has been noticed with an increase in $[\text{KBrO}_3]$ and [GA] while the number of oscillations (n) increase with an increase in $[\text{KBrO}_3]$ and [GA]. Such trends are in accordance with the concentration effect on the rate of reaction. A substantial increase in the [Mn(II)] and/or $[\text{H}_2\text{SO}_4]$ increases not only the time of initiation but also the T_p , which may

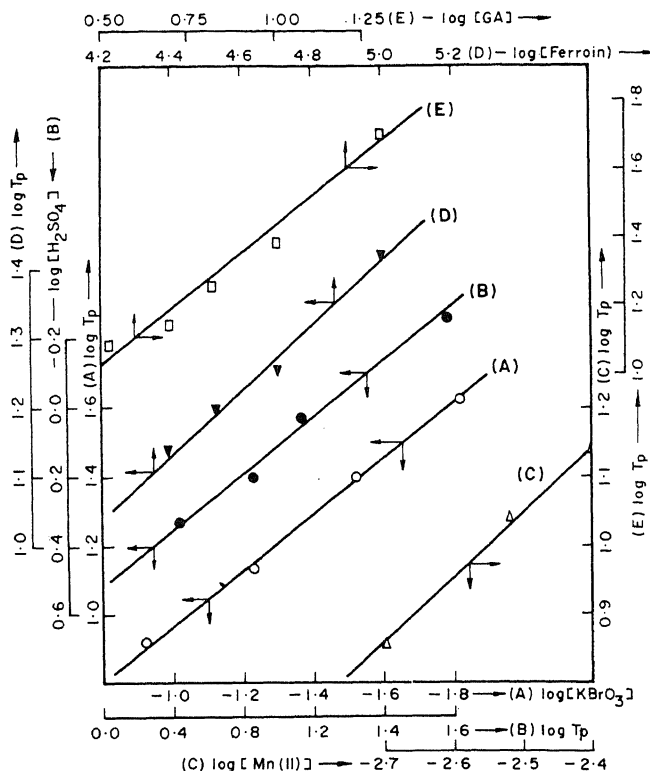


Figure 3. Characteristics of chemical waves in glycollic acid system at 300 K. (A) Plot of $\log T_p$ vs. $\log [\text{KBrO}_3]$: $[\text{H}_2\text{SO}_4] = 1.07 \text{ mol dm}^{-3}$; $[\text{Mn(II)}] = 0.004 \text{ mol dm}^{-3}$; $[\text{Ferrein}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{GA}] = 0.200 \text{ mol dm}^{-3}$; (B) Plot of $\log [\text{H}_2\text{SO}_4]$ vs. $\log T_p$: $[\text{KBrO}_3] = 0.060 \text{ mol dm}^{-3}$, other conditions as in plot A; (C) Plot of $\log T_p$ vs. $\log [\text{Mn(II)}]$: $[\text{H}_2\text{SO}_4] = 1.07 \text{ mol dm}^{-3}$, other conditions as in plot B; (D) Plot of $\log T_p$ vs. $\log [\text{ferrein}]$: $[\text{GA}] = 0.200 \text{ mol dm}^{-3}$, other conditions are same as in plot C; (E) Plot of $\log T_p$ vs. $\log [\text{GA}]$: $[\text{ferrein}] = 4 \times 10^{-5} \text{ mol dm}^{-3}$, other conditions as in plot D.

Table 2. Empirical analytical relationships in glycollic acid system at 300 K.

Reactant	Concentration range (mol dm^{-3})	Empirical equation
KBrO_3	0.015–0.120	$T_i = 89.12/[\text{KBrO}_3]^{0.18}$ $T_p = 1.58/[\text{KBrO}_3]^{0.81}$
H_2SO_4	0.534–3.204	$T_i = 151.36/[\text{H}_2\text{SO}_4]^{1.32}$ $T_p = 12.88/[\text{H}_2\text{SO}_4]^{1.75}$ $T_i = 380.18/[\text{H}_2\text{SO}_4]^{2.25}$
GA	0.050–0.300	$T_i = 81.28/[\text{GA}]^{0.58}$ $T_p = 4.074/[\text{GA}]^{0.90}$ $T_i = 263/[\text{GA}]^{0.70}$
Mn(II)	0.001–0.004	$T_i = 3.70/[\text{Mn(II)}]^{0.66}$ $T_p = 2.7 \times 10^3 [\text{Mn(II)}]^{0.95}$
Ferrein	1×10^{-5} – 4×10^{-5}	$T_i = 2.88 \times 10^4 [\text{Ferrein}]^{0.52}$ $T_p = 234/[\text{Ferrein}]^{0.85}$

be probably due to the stabilisation of the Mn(III) species in higher acid concentrations. However, an increase in [ferroin] decreases T_i and T_p thus showing its catalytic activity which may be mainly attributed to the II-electron cloud present in the ring system of the phenanthroline moiety (Taube 1955).

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Erratum

The date of receipt of the following article was not printed in the journal. We regret the omission.

“High T_c superconductivity in oxides derived from $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ ”

by P GANGULY and C N R RAO

Proc. Indian Acad. Sci. (Chem. Sci.), Vol. **97**, pp. 631–633 (1986)

Date of receipt: 2 February 1987

Foreword

The importance of the hydrophobic effect began to be first realised in colloid chemical studies on the formation of soap molecule aggregates. Its role as a determinant in biopolymer structures was appreciated and commented upon with some rigour some thirty years ago. The early sixties saw a lot of activity in the area particularly focussed on globular protein structures and interactions and also a revival of interest on micelles. Charles Tanford has been one of the trend-setters in quantitatively analysing the hydrophobic effect and its consequences since those days. The first monograph on the hydrophobic effect was written by him in 1973 and has gone through a second edition in 1980. It is thus particularly appropriate that Professor Tanford starts our "Symposium in Print" with a perspective overview. This overview contains information that is interesting, stimulating and provocative. For example, Tanford points out that had Benjamin Franklin done some mental "kite flying", he would have been the first to measure molecular sizes.

The second article is from Arie Ben-Naim, who has done much to aid our understanding of the thermodynamic and statistical mechanical basis of the hydrophobic effect through his earlier papers and his 1980 monograph on hydrophobic interactions. This is the first time the importance of solvent-induced effects is being discussed in the context of hydrophobic interactions.

The distance-dependence of the hydrophobic force between surfaces is only recently becoming delineated. We are fortunate that one of the pioneers in these measurements, Dr Pashley, has contributed a paper specifically on this topic. Jacques Desnoyers has been concerned over the years with thermodynamic aspects of solvation, hydrophobic hydration and hydrophobic association. Roux and Desnoyers have analysed micellar type equilibrium models for alcohol:water mixtures.

The influence of hydrophobic forces on chemical reactivity is a subject of great interest. Xi-Kui Jiang and associates had earlier provided compelling evidence for the self-coiling of long chain ester molecules by studying their solvolysis rates. In one of their papers, they show that lipophilic forces are important while in another paper the competition between aggregation and amylose-wrapping of long chain esters is studied. The concept of the critical aggregation concentration that they have introduced might have other applications as well.

V Ramamurthy has written an interesting article on the hydrophobic cavities that the cyclodextrins offer to guest molecules and the use of these pockets as unique media to do photochemical reactions of organic chemical interest. We also have two papers on micellar aggregates. The differences in the microenvironment offered to a solubilizate in micelles of different structures and packing arrangements have been presented in one paper. This is a fine-structural comparison between micelles and is novel since until now all micelles have been thought of and treated as aggregates that provide a hydrophobic interior for housing guest molecules. The paper by Puranam and Balaram carries us into the realm of

biomolecules and treats an important problem of metabolite solubilization and clearance. The paper offers an insight into the mode of solubilization of the pigment bilirubin in bile salt assemblies and the intimate proximal interactions that occur between the solubilizate and the host molecules. The last paper by R. Nagaraj is concerned with the role of the hydrophobic leader sequence that occurs in proteins destined for transport across membranes. What are the signals that are built into these molecules that tell them to cross the membrane—and how do these signal segments interact with the membrane?

As mentioned earlier, this issue is a "Symposium in Print". The authors did not meet formally but offered to contribute to a common theme. We thank all the invited authors for their enthusiasm for the idea, their promptness, and for putting up with some protracted correspondence that must have tried their patience.

D BALASUBRAMANIAN
Guest Editor

C N R RAO
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Organizational consequences of the hydrophobic interaction

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Abstract. If otherwise hydrophobic molecules also contain hydrophilic groups, they become known as "amphiphilic" and they are then subject to a potent organizational effect, which orients each molecule so as to satisfy as far as possible the thermodynamic requirements of both parts of the molecule. One consequence is the formation of monolayers of oil on water, which has been of great historical importance in physics and chemistry, leading to the first determinations of molecular size, symmetry and flexibility. The most important role of this kind of organizational force, however, is in biology. Here amphiphilic phospholipid molecules are organized into bilayers that are essential to the very existence of a living cell, defining the boundary between the inside of a cell and its environment. The formation of specific structures of proteins, too, is dominated by the hydrophobic interaction: in this case the need to fold the protein in such a way (intricately, with many twists and turns) as to minimize contact between hydrophobic groups and the surrounding aqueous medium. It is not an exaggeration to say that hydrophobic interactions are essential for all aspects of the chemistry of life as we know it.

Keywords. Monolayers; bilayers; lipids; molecular dimension; living cells; proteins.

1. Introduction

The "hydrophobic effect" as a topic in physical chemistry – how to account for the unusual thermodynamic attributes of aqueous solutions of hydrocarbons and certain other poorly soluble solutes – would by itself be a rather academic subject, of interest to relatively few scientists. The effect happens however to be a major factor in the creation of a potent force for structural organization. The existence of this force has played an important role in the history of physics and chemistry, in the development of clear ideas about the nature of molecules. Its ability to generate spatial organization, with molecules all oriented the same way, made it possible to "see" molecular properties with a clarity that is not possible for unoriented molecules.

Structural organization based on the hydrophobic effect has proved more recently to be even more important in biology, where it is used by nature itself to create structural organization. The very existence of a living cell, the definition of a boundary between the inside of a cell and its environment (irrespective of what the contents of the cell may be) is absolutely dependent on the hydrophobic effect. And within the cell, the existence of enzymes and transport proteins with highly specific functions is likewise absolutely dependent on the influence of hydrophobic interactions. The phenomenon that forms the subject of this volume is essential for virtually every aspect of life.

I shall focus in this paper on this organizational effect, partly in historical fashion, beginning with the first recorded observation of it by Benjamin Franklin more than 200 years ago.

the pond at Clapham Common outside London he did so, using olive oil that you could buy at any grocery store.

And it worked. Just a teaspoonful was enough. It was a windy day and the surface of the pond was rough, but the oil produced an instant calm over a space of several square yards, which extended itself gradually until an area that Franklin estimated to be about half an acre became, in his own words, "as smooth as a looking glass".

He repeated the experiment many times, often for the edification of friends or fellow-scientists, and it always worked. What is remarkable, however, is that Franklin had (in spite of being relatively untutored) an excellent scientific insight and realized right from the start that the calming of the water was not the most interesting part of the phenomenon he was observing. The intriguing part was the *spreading* of the teaspoonful of oil to such a large area. In his own words (Franklin 1774).

"In these experiments, one circumstance struck me with particular surprise. This was the sudden, wide and forcible spreading of a drop of oil on the face of the water, which I do not know that anybody has hitherto considered. If a drop of oil is put on a polished marble table, or on a looking glass that lies horizontally; the drop remains in place, spreading very little. But when put on water it spreads instantly many feet round, becoming so thin as to produce the prismatic colors, for a considerable space, and beyond them so much thinner as to be invisible, except in its effect of smoothing the waves at a much greater distance."

And he puzzled over it. There are oil particles and water particles. You put some oil particles on a smooth surface like a looking glass placed horizontally, and the oil doesn't spread. And you put water on the same surface, it doesn't spread either. But you put the oil particles on top of the water particles, and you get this extraordinary spreading to a huge area. (If you calculate it, the spreading factor here is 10^7 !). He puzzled about it, but could not come up with an answer.

And we cannot blame Franklin for this because the time was not ripe for a correct molecular interpretation. As I said earlier, the concept of a "molecule" as the smallest particle with the chemical attributes of a substance was accepted. But it is natural to assume that these defining attributes would be distributed uniformly throughout the mass of the molecule, that every part of each molecule would have the same properties as the bulk substance from which it was derived. The idea that an olive oil molecule could be composed of distinct domains – attracted to water at one end and repelled by it at the other end – could not have been conceived.

It is precisely what is *essential* for an explanation of the spreading.

It requires the simultaneous presence of both attractive and repulsive forces. The attractive force to make sure that each oil molecule is at least partially dissolved in the water, the repulsive force to make sure that at least a part of the molecule remains outside the water. Only in this way can a monomolecular film be formed.

When the film is first formed, it is difficult to imagine how the enormously thin film can be anything other than a monolayer. It is clear that there is no interaction between oil molecules, for otherwise there would not be a compact film of oil to start the experiment. And the spreading on water does not continue indefinitely, as both Franklin and subsequent observers reported. There comes a point when the spreading stops, when the film has reached some kind of limit.

where the molecule must move, with its hydrophilic part in the water and its hydrophobic part out of the water. If no interface is available, then the molecule must create its own interface – concerted action among an assembly of amphiphilic molecules becomes necessary to create a volume within the system, within which the hydrophobic parts of the molecule can be in contact with each other and shielded from contact with water.

It is worth noting that these simple consequences of the structure of an amphiphilic molecule or ion depend on an aspect of the hydrophobic interaction that is often not greatly stressed – the fact that water molecules are very small. It is an excellent approximation, not only conceptually but almost quantitatively, to look upon the domains of amphiphilic molecules as nearly independent of each other in their interactions with water. This would not be possible if a water molecule were not small compared to the size of the domains.

3. Benjamin Franklin: Oil on troubled waters

The first scientific report of this powerful organizing effect came from Benjamin Franklin in 1774 (Franklin 1774). Franklin was in London on a diplomatic mission, trying to negotiate an agreement between the King's government and a few of the American colonies to redress grievances that had to do with fiscal matters – taxes and import duties. However, he had no legal standing as a diplomat because only foreign countries could have “ambassadors” with access to the King and Privy Council. The American colonies were part of England, ruled by Governors appointed by the Crown, one for each colony, their positions not unlike the position of the Viceroy in India a century later. Mere citizens were not supposed to go to London to bargain directly with the authorities, even when they were sent by local governing bodies at home, but were supposed to approach the government through the proper channels. Needless to say, progress in processing Franklin's petitions was slow, and he had plenty of time for travel and other activities.

Though diplomatically without status, Franklin did have an honorable standing in England as a scientist. In this respect the perception of America as English “property” helped him. Franklin was a Fellow of the Royal Society, an organization open only to British citizens, having been elected while he was still in Philadelphia, on the basis of his brilliant work on electricity. He had also been awarded the Royal Society's prestigious Copley Medal for this work. He was therefore welcomed by the scientific community when he came to England, as someone already well known to them from his publications. Most of his friends and associates during his many years in England were in fact scientists or philosophers. He was a regular attendee at Royal Society meetings, and was often consulted and befriended by younger scientists, such as Joseph Priestley.

There were still people in England at that time who did not believe in molecules, but Benjamin Franklin certainly did. He was a Newtonian and, like most English scientists, believed in “ultimate particles” of matter, which is what molecules are. But when he did the experiment that led to his 1774 paper he wasn't (at first) thinking about molecules at all, but about the age-old practice of mariners to pour oil on troubled waters – vegetable or fish oil was supposed to calm the waves in a storm. Franklin was skeptical, but he wanted to try the experiment, and one day on

the pond at Clapham Common outside London he did so, using olive oil that you could buy at any grocery store.

And it worked. Just a teaspoonful was enough. It was a windy day and the surface of the pond was rough, but the oil produced an instant calm over a space of several square yards, which extended itself gradually until an area that Franklin estimated to be about half an acre became, in his own words, "as smooth as a looking glass".

He repeated the experiment many times, often for the edification of friends or fellow-scientists, and it always worked. What is remarkable, however, is that Franklin had (in spite of being relatively untutored) an excellent scientific insight and realized right from the start that the calming of the water was not the most interesting part of the phenomenon he was observing. The intriguing part was the *spreading* of the teaspoonful of oil to such a large area. In his own words (Franklin 1774).

"In these experiments, one circumstance struck me with particular surprise. This was the sudden, wide and forcible spreading of a drop of oil on the face of the water, which I do not know that anybody has hitherto considered. If a drop of oil is put on a polished marble table, or on a looking glass that lies horizontally; the drop remains in place, spreading very little. But when put on water it spreads instantly many feet round, becoming so thin as to produce the prismatic colors, for a considerable space, and beyond them so much thinner as to be invisible, except in its effect of smoothing the waves at a much greater distance."

And he puzzled over it. There are oil particles and water particles. You put some oil particles on a smooth surface like a looking glass placed horizontally, and the oil doesn't spread. And you put water on the same surface, it doesn't spread either. But you put the oil particles on top of the water particles, and you get this extraordinary spreading to a huge area. (If you calculate it, the spreading factor here is 10^7 !). He puzzled about it, but could not come up with an answer.

And we cannot blame Franklin for this because the time was not ripe for a correct molecular interpretation. As I said earlier, the concept of a "molecule" as the smallest particle with the chemical attributes of a substance was accepted. But it was natural to assume that these defining attributes would be distributed uniformly throughout the mass of the molecule, that every part of each molecule would have the same properties as the bulk substance from which it was derived. The idea that an olive oil molecule could be composed of distinct domains – attracted to water at one end and repelled by it at the other end – could not have been conceived.

But that is precisely what is *essential* for an explanation of the spreading phenomenon. It requires the simultaneous presence of both attractive and repulsive forces, the attractive force to make sure that each oil molecule is at least in part immersed in the water, the repulsive force to make sure that at least a part of each molecule remains outside the water. Only in this way can a monomolecular film be formed.

And, it might be observed, it is difficult to imagine how the enormously spread-out film can be anything other than a monolayer. It is clear that there is cohesiveness between oil molecules, for otherwise there would not be a compact "drop" of oil to start the experiment. And the spreading on water does not continue indefinitely, as both Franklin and subsequent observers reported. There comes a point when the spreading stops, when the film has reached some kind of limit.

What other interpretation can there be than that the limit represent a layer of the ultimate oil particles – when no further expansion could occur without disrupting the last bit of the force of attraction between these particles?

4. Molecular dimensions

There is one puzzle, which has not been satisfactorily answered. Ben Franklin knew that a drop of oil, when spread out over an area of half an acre, becomes astonishingly thin, thin enough for us to observe the prismatic colors, and even thinner than that, where the presence of the oil would have been undetectable but for the smoothing of the waves. But he did not calculate precisely how thin, and nobody really understands why. He was a practical man, accustomed to weights and measures, and certainly knew how to make the calculation: given that he had a teaspoonful (2 cc) and that it spread to an area of half an acre (2000 m²), he would have arrived at the incredibly low value of 10⁻⁷ cm for the film thickness – less than one ten millionth's of an inch is what Franklin would have said.

Anyway, he didn't make the calculation. If he had done so, he would surely also have realized that 10⁻⁷ cm must be about the value of the dimensions of the olive oil molecule – or at least that the molecule could not possibly be larger than that. Had Franklin done so, his paper would have come down in history as one of the great classics – the first measurement of molecular size! Although the *existence* of “ultimate particles” was fairly generally accepted, nobody had the slightest idea what size they would turn out to be.

As it happened, Franklin's method – reduced to laboratory scale – was in fact the method by which molecular dimensions were first measured directly. But it didn't happen till 100 years later, when Lord Rayleigh repeated the experiment, which he did deliberately for the purpose of determining molecular dimensions. “In view of the great interest which attaches to the determination of molecular magnitudes,” he said, “the matter seemed well worthy of investigation.” And investigate it he did (Rayleigh 1890).

For quantitation, in his own laboratory, Rayleigh at first used a circular bath with a diameter of about 1 meter, and he used the motion of camphor chips as a measuring device. The chips move about spontaneously on an uncontaminated water surface, but motion ceases where the surface is covered by oil. The thickness measurement that Rayleigh reported required successive measurements with increasing amounts of oil until he reached a volume of oil that was “about enough” to “very nearly stop” all movement of the camphor.

About the same time Agnes Pockels made the same measurement, but she did it better (Pockels 1891). She invented the prototype of what is now known as a “Langmuir trough”, a shallow *rectangular* container with movable strips that can be used both to sweep surfaces clean of impurities and also to compress or expand the film at will while keeping the amount of adsorbed material constant. Pockels used surface tension as a measure of the state of the surface, while Langmuir later used lateral surface pressure, but the two quantities are related by an equation: the important aspect was that measurements could now be made reversibly and continuously over a wide range of areas for a single application of oil.

Agnes Pockels was one of the most remarkable woman scientists of all time

(Giles and Forrester 1971). She was a young lady without formal education, who did all of her work in her own kitchen, in Braunschweig, Germany, with home-made equipment. The idea for sweeping an aqueous surface to keep it clean apparently came to her from the kitchen technique of skimming fat off the top of soup or stew. She had no idea whether or not her amateur work on surface physics had any value, and didn't receive much encouragement from colleagues of her brother's, who was a professor of physics at the University of Göttingen. Then her brother saw Lord Rayleigh's paper on oil films in the Proceedings of the Royal Society, and showed it to his sister. She then had the courage to write to Rayleigh about her own work, and he immediately recognized its value. He helped her to get her technique and results published in *Nature*, and himself copied her apparatus and used it for his own later measurements.

As table 1 shows, all the data for the thickness of an olive oil monolayer are in good agreement, including that derived from the later work of Irving Langmuir, who of course measured more than just film thickness. Note that Avogadro's Number was not yet known at the time of Rayleigh and Pockels, so that they both determined film thickness from the ratio of total volume to total surface area. Avogadro's number was established by the time of Langmuir, so that he knew how many molecules he had in the amount of oil he placed on the surface, and could report his results directly in molecular dimensions.

5. Molecular shape and orientation

It is rather curious that Rayleigh himself was blind to aspects of his experiment other than the one dimension he reported. In spite of his stated great interest in the "determination of molecular magnitudes", he appears not to have speculated at all about molecular *shape*. The structural formulas for organic molecules are only representations of how atoms are linked to each other, and cannot tell us anything about the disposition of the atoms in space. The molecules of oil on water might be long and thin, imitating in nature the way we write the formulas on paper. But it makes equally good sense to think that the molecules might be coiled up into compact balls to occupy minimal space. (Protein molecules with incredibly long chains – thousands of atoms – in fact do that, as we shall mention below.) Rayleigh did not discuss this problem in his papers. It was Irving Langmuir who addressed himself to the problem and thereby in effect introduced the modern concept of molecular "conformation" (Langmuir 1917).

Table 1. Thickness of a fully extended film of olive oil on water.

	Amount	Area	Film thickness (Å)
B Franklin (1774)	1 teaspoon (2 cc)	1/2 acre	10
Lord Rayleigh (1890)	0.8 mg (0.0009 cc)	5500 cm ²	16
Agnes Pockels (1892)	1.0 mg (0.0011 cc)	8460 cm ²	13
I Langmuir (1917)	—	—	13

Table 2. Molecular dimensions from surface area measurements.

	Cross-sectional area (Å ²)	Square root of same (Å)	Length (Å)
Palmitic acid (C16)	21	4.6	24
Stearic acid (C18)	22	4.7	25
Tristearin	66	8.1	25
Oleic acid (C18)	46	6.8	11.2
Triolein	126	11.2	13

From Langmuir 1917.

Some of Langmuir's results are shown in table 2. They give for the first time real information about molecular asymmetry – information that can be obtained only because the molecules are all identically oriented at the air/water interface. They confirm the conceptual thinking that explains the orientation, that it arises from the opposing needs of the hydrophobic and hydrophilic ends of the molecules. For example, tristearin has the same molecular length as stearic acid, but three times the cross-sectional area, as expected on this basis. The absolute numbers provided for the first time an experimental measure of hydrocarbon chain flexibility: molecular lengths are less than expected for fully extended chains. The difference between oleic acid and stearic acid illustrates the influence of the double bond.

Today we are accustomed to seeing molecular "pictures", based on model building or x-ray diffraction studies of crystals. In 1917, such sophisticated tools were not available. Langmuir's measurements on hydrophobically oriented films thus had a truly revolutionary impact at a time when understanding of molecular structure was virtually non-existent.

6. Modern use of monolayers

The ability to produce so easily layers of molecules that have a unique orientation in space continues to be exploited by chemists to the present day. And, by some strange quirk, monolayer experimentation has involved at least one other prominent person like Benjamin Franklin, whose first claim to fame is in geopolitics rather than in science. In the modern era this is Margaret Thatcher, the Prime Minister of Britain. She started her professional life as a chemist, and wrote a respectable paper (under her maiden name of Margaret Roberts) on a comparison between the kinetics of ester hydrolysis in a monolayer (similarly oriented molecules side-by-side) and in bulk solution. She found no significant difference in activation energy, though the absolute rates, of course, were different (Jellinek and Roberts 1951).

More recent monolayer work includes spectral studies, where the defined orientation of adjacent chromophores helps to define the interaction between them more precisely (Möbius 1981), and experiments to discriminate directly between stereo-isomers in intermolecular forces (Arnett *et al* 1982).

7. Importance for Biology

By the year 1900 it was known that living organisms are composed of "cells". Many microscopic organisms – bacteria, yeasts, amoeba – are unicellular, all their life functions contained within a single cell. The visible plants and animals around us, however, contain millions or billions of cells, functionally differentiated, so that the organism is capable of a much more complex life.

Life originated in the ocean, and water remains to this day the universal medium for living things. Thus all the cells of multicellular organisms are bathed in an aqueous extracellular fluid, usually a rather salty fluid, with a very high content of Na^+ , and millimolar levels of Ca^{2+} and Mg^{2+} . The internal volume of cells is likewise aqueous, but does not usually contain the same inorganic salts as the extracellular medium: K^+ is the most abundant cation instead of Na^+ , and levels of Ca^{2+} are extremely low, usually below $1\ \mu\text{M}$. This difference in salt composition is one of the manifestations of "life", but it is of course only a small part of the difference between the inside and outside of cells. All the machinery for life, all the metabolites for energy production, amino acids for protein synthesis and the proteins they build, and the nucleic acids that carry the genetic information – all these substances are inside the cell and must be kept there, must not be allowed to escape.

It is clear – and was clear to most people by the year 1900 – that cells must be defined by *membranes*, by thin films that enclose the cell contents and prevent mixing with the external solutions. But the chemical nature of membranes was not yet known.

In the year 1899 Charles Ernest Overton investigated the question (Overton 1899). He investigated the permeability characteristics of muscle cell membranes by studying substances to which the membranes were in fact quite permeable (alcohols, for example). His most important discovery was a striking correlation between membrane permeation rates and solubilities in – surprisingly, olive oil! This discovery led to several more or less obvious conclusions:

1. There must be some resemblance between a cell membrane and olive oil. The membrane must be impregnated with molecules of the same class as the olive oil molecule – either fats or lipids.

2. The correlation with a "solubility" measurement suggests (perfectly reasonably) that the way molecules get across the membrane is by first dissolving in the membrane interior, then diffusing across the membrane thickness, and, finally entering the aqueous medium on the other side. And that the ability to dissolve in the lipid-like interior is the critical factor, limiting how fast the overall process can occur.

3. This mechanism provides, for the first time, a simple explanation for the vital function of the membrane – enclosure and confinement of the cell contents. The molecules (and the inorganic cations) that need to be confined are mostly water-soluble, strongly hydrophilic. Their solubility in olive oil is slight. By inference their solubility in the membrane interior is also low, and this explains the low rate of escape from the cell.

Overton (1899) was astute enough to realize that "containment" could not by itself suffice to define a viable membrane. The substances to be contained must be brought in from the outside, and the already mentioned differences in salt

concentrations must be continuously maintained. Inward transport often needs to be "uphill", from low concentration to high concentration, contrary to the direction of spontaneous diffusion, which requires expenditure of metabolic energy, specially designed engines to use energy for this unique purpose. Overton realized that that these processes represent a problem quite separate from the problem of containment. "This must be a phenomenon quite different from the simple diffusion of substances through the protoplasts", he said.

And it was soon realized that a real living membrane had to be a mosaic surface, containing proteins for communication across the membrane, as well as lipid for containment. About the same time, lipid chemists discovered that the particular lipids involved in membrane formation were principally *phospholipids* (figure 1), or similar lipid types with two fatty acid chains per glycerol moiety. The structural advantage of having the third position occupied by a strong polar group is to magnify the need that one side of the molecule remains in contact with water. The hydrophilic groups of oils and fats are only weakly hydrophilic, and cells that store oils and fats as food reserves commonly contain globules of lipid in which the many lipid molecules have no contact with water. For phospholipids the thermodynamic cost of incorporation into such globules would be prohibitively high.

8. Gorter and Grendel. Recognition of the lipid bilayer

Evart Gorter, a Dutch pediatrician, accepted the fact that cell membranes were composed of lipids, and, when he read Irving Langmuir's paper after World War I, immediately saw what it implied for cell membranes (figure 2). The membrane's function is to divide one aqueous compartment from another aqueous compartment, a physical situation quite different from that at Langmuir's air/water interface. Here the lipid hydrocarbon tails must avoid the water on *both sides* of the membrane. The only way to accomplish that is to have the ionic lipid head groups (which of course need to be hydrated) *facing the water on both sides*. The membrane must be a *bimolecular* layer. There is no rational way to accommodate "extra" lipid molecules (more than needed for the bilayer) within the bilayer's hydrocarbon interior.

Gorter had to wait several years (until his appointment as Professor of Pediatrics) before he was allowed to have a laboratory in which this conclusion could be tested. Then, in 1925, with the help of a student, F Grendel, he carried out one of the great experiments in the history of biology (Gorter and Grendel 1925). Gorter and Grendel extracted all the lipids from the membranes of red blood cells, and measured their surface area when spread as a monolayer on water. They then compared this with the surface areas of the cells themselves, based on microscope pictures. Some of their results are shown in table 3. The conclusion is clear. There is a difference of exactly a factor of two, independent of whether one is using animals with large or small red blood cells. The cell membrane must be a *bilayer*, exactly two lipid molecules thick.

It is remarkable how much time elapsed before this now seemingly obvious principle was generally accepted. Experimentalists looking at membranes through early versions of the electron microscope had insufficient resolution to be very exact about membrane thickness, and, as late as the mid-1950's, a theoretically



Figure 2. Schematic diagrams of a lipid monolayer and bilayer. Black circles represent hydrophilic ends of the lipid molecules, wavy lines the hydrocarbon chains. The pictures are cross-sections, lacking a third dimension. Both monolayers and bilayers normally occur as extended surfaces. Bilayers tend to fold upon themselves to eliminate the peripheral edge, creating closed vesicles with an internal water-filled space.

The thermodynamic driving force that dictates the orientation of lipid molecules at an interface is the need for the hydrophilic end of each molecule to be dissolved in the water, and the simultaneous need for the hydrocarbon chains to be excluded from water. At the interface between two aqueous solutions, hydrophilic groups must face *both sides* of the layer—a bimolecular film is a necessity. The pressure exerted by the water on the two sides holds the two halves of the bilayer tightly together.

Table 3. Typical results of Gorter and Grendel (1925).

	Amount of blood used for analysis (gm)	No. of cells per mm ³	Surface of one cell (μ ²)	(A) Surface of total cells used in expt. (m ²)	(B) Monolayer surface of lipids (m ²)	Ratio B/A
Dog A	40	8,000,000	98	31.3	62	2
	10	6,890,000	90	6.2	12.2	2
Sheep 1	10	9,900,000	29.8	2.95	6.2	2.1
	9	9,900,000	29.8	2.65	5.8	2.2
Rabbit A	10	5,900,000	92.5	5.46	9.9	1.8
	10	5,900,000	92.5	5.46	8.8	1.6
	0.5	5,900,000	92.5	0.27	0.54	2
Rabbit B	1	6,600,000	74.4	0.49	0.96	2
	10	6,600,000	74.4	4.9	9.8	2
	10	6,600,000	74.4	4.9	9.8	2

questionable model by Danielli and Davson (1935), dominated the thinking of biologists about the arrangement of the constituents of cell membranes. The Danielli-Davson model's thickness was left *unspecified*: layers of three lipid molecules were considered as likely as bilayers. Moreover, the Danielli-Davson model had protein coating the *outside* of the lipid layers, where it could not have catalyzed the transport function required for physiological viability.

9. Proteins

Proteins are the catalysts that create and maintain the chemistry of life. Every biological reaction, some of them exquisitely specific, some of them impossible to duplicate in the laboratory, is made possible by specific group configurations on the

surface of a protein molecule. There are thousands of different proteins, each precisely tailored to its task.

The basic structure of proteins is quite simple. Each protein is a "chain polymer", made from hundreds of amino acid units, as shown in figure 3. Twenty different kinds of amino acids (different "R" groups in the diagram) are used in nature, arranged for each protein in a strictly defined sequence. Variations in the length of the chain, variations in composition (constituent amino acids), and, especially, variations in sequence, clearly permit the generation of virtually an infinite number of distinct molecules. The protein molecules that *actually* exist are genetically determined and synthesized error-free – there is nothing random or statistical in the synthetic process.

The twenty amino acids that enter into protein formation include some that donate ionic and highly polar side chains, and also some that provide hydrophobic side chains. Table 4 lists some of the more important of the latter. These hydrophobic entities of the molecule, though quite small relative to the long hydrocarbon chains of the molecules pictured in figure 1, make an extended structure of the protein chain, everywhere in contact with solvent, thermodynamically unstable. Because hydrophobic side chains are distributed all along the chain they cannot be removed from contact with water by any simple universal structural organization. What must happen instead is that the chain must coil into a compact "globular" structure with a complex pattern of twists and turns, so as to shield as many hydrophobic entities as possible from the solvent, while at the same time keeping hydrophilic side chains on the outside in contact with water. Exactly how this is done – the ultimate three-dimensional folding – is unique to each individual protein. For the majority of arbitrarily chosen sequences (by a computer, for example) there is probably no way to achieve the desired result at all, but, as I have said, there is nothing arbitrary about the protein sequences that exist. Ones that cannot fold to a compact structure have not survived the evolutionary process.

It should be noted that the backbone of the chain structure, the continually repeated peptide group, is obviously hydrophilic. However, it is capable of internal hydrogen-bonding that can satisfy the requirements of polarity without absolute necessity for contact with water. The well-known " α -helix" is the most frequent example. It is probable that the transition between an open chain, with each peptide group bonded to water molecules, and a cooperative water-free internally hydrogen-bonded structure, makes almost no contribution to thermodynamic balance between an overall unfolded structure and a specifically folded three-

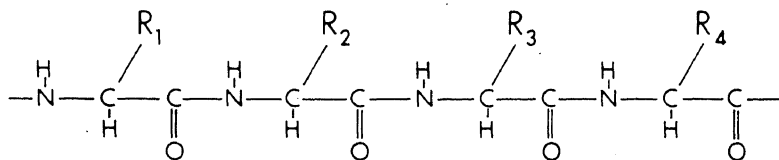


Figure 3. Chemical formulas for protein molecules. Each molecule is a "chain polymer", made from hundreds of amino acid units. Twenty different amino acids (different "R" groups in the diagram) are used in nature, arranged for each protein in a strictly defined sequence. Some of the amino acids provide ionic or highly polar side chains, some are hydrophobic.

Table 4. Typical hydrophobic side chains (R Groups of figure 3)

$-\text{CH}_3$	Alanine
$-\text{CH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array}$	Valine
$-\text{CH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_2-\text{CH}_3 \end{array}$	Isoleucine
$-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_3$	Methionine
$-\text{CH}_2-$ 	Phenylalanine

dimensional organization. The internalization of hydrophobic groups is probably the major thermodynamic factor.

It might also be mentioned that the small size of the hydrophobic side chains permits the existence of imperfections, i.e., the thermodynamic cost of leaving an occasional hydrophobic group in contact with water is dependent on the area of contact with water, and in the case of protein side chains is therefore relatively small. If 100% sequestration of hydrophobic groups were required, then it might not be possible to find any structure that would satisfy the thermodynamic requirements within the constraints of allowed bond distances, bond angles and hydrogen-bond orientations along the macromolecular backbone.

The beautiful patterns of folding that result from the need to satisfy the hydrophobic and hydrophilic thermodynamic driving forces have been described in many places: a good recent summary is given by Richardson (1981). What is important here is not the beauty of the ultimate structures, but the catalytic functional specificity that results from it. Because the overall manner of folding is unique, it rigidly locks the hydrophilic groups at the surface into unique arrangements that can serve as sites for recognizing and binding specific ligands, or as catalytic centers for making and breaking organic chemical bonds.

10. Proteins in membranes

The typical enzyme or binding protein envisaged in the preceding paragraph is water-soluble by virtue of the hydrophilic amino acid side chains that cover its surface – the specific binding or catalytic site *per se* involves only a small part of the surface. But proteins must also be part of functioning biological membranes, and some of them must traverse the membrane from one side to the other in order to provide for regulated communication between the internal aqueous medium of a cell (the so-called “cytoplasm”) and the extracellular medium, or between the cytoplasm and otherwise sealed-off intracellular compartments, such as mitochondria and the endoplasmic reticulum. The specific proteins involved here must have part of their surface, after folding, in contact with the hydrocarbon chains of the

interior of a membrane bilayer. Indeed, this turns out to be the case. Membrane-incorporated proteins, just beginning to be studied in detail, do not have wholly hydrophilic surfaces, but contain segments that reside preferentially in a non-aqueous medium. Figure 4 provides a schematic illustration.

All proteins, including membrane proteins, are synthesized within the cell, i.e., on the cytoplasmic sides of membranes. How membrane proteins are actually incorporated into phospholipid bilayers, with some hydrophilic part of each molecule on both sides of the membrane, remains an unsolved problem. The important thermodynamic feature is that the proteins we actually find in membranes are thermodynamically stable once located there, by virtue of appropriately designed segments of hydrophobic surface. A protein with a wholly hydrophilic surface would be unstable in the membrane, no matter what the mechanism whereby it arrived there, and would spontaneously seek an entirely aqueous environment. Thermodynamics has priority over other aspects of biochemical mechanism.

11. Micelles and emulsions

There is still another kind of molecular organization that amphiphilic molecules can undergo, namely the formation of micelles or emulsions, aggregates of many small molecules, in principle like phospholipid bilayers with a hydrophobic interior and a hydrophilic surface, differing from bilayers in that the surfaces are curved, generating aggregates of limited size instead of extended sheet-like structure. The basis for this difference rests on molecular geometry: the relation between the size of the hydrophilic end of an amphiphile molecule and the molecular volume of the hydrocarbon portion (Tanford 1978).

Micelles and emulsions are of great importance industrially and socially (soaps and detergents), but they are also used in biological systems, in the handling of facts by living organisms, e.g., in the absorption of fats by the gut in mammalian digestion. Micelle-forming detergents are also used as reagents by biochemists who want to break up biological membranes so as to be able to study individual

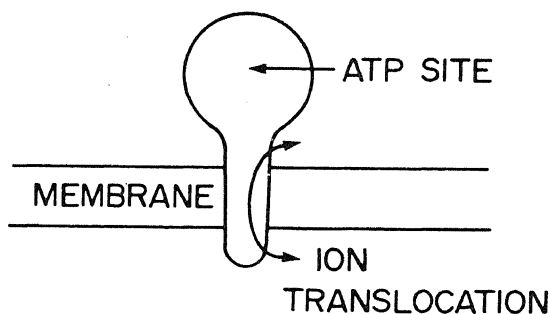


Figure 4. Schematic representation of a protein molecule incorporated into a biological membrane. The segment of the protein in contact with the bilayer interior has a surface made up of hydrophobic amino acid side chains (table 4) and is firmly anchored in the membrane by the hydrophobic exclusion from the bulk media on either side. Functionally, the protein is intended to represent an "ion pump", a catalyst that energetically couples ATP hydrolysis to uphill transport of cations (Ca^{2+} or Na^{+}).

membrane proteins or other components, but want to maintain the existence of a hydrocarbon/water interface similar to that of the native membrane (Tanford and Reynolds 1976).

Because of their practical importance, the substances that form micelles and emulsions (loosely termed "surfactants") are much better known to chemists than are lipids and proteins (see, for example, Tanford 1980), and for that reason I have not discussed them in this paper. It should be noted that the most recent international symposium on surfactants in fact took place in India, and the proceedings are in press.

12. Discussion

One might ask the question, why has Nature chosen the hydrophobic effect as the mechanism whereby it achieves the super-molecular organization without which Life could not exist at all? The probable answer lies in the fact that life originated in water and has continued to evolve in an aqueous environment. It is economical to employ the means already at hand and that's what has happened here. A similar phenomenon is apparent with respect to signalling across membranes (by means of proteins that span the membrane). Na^+ , K^+ and Ca^{2+} ions are used for most such trans-membrane signalling, the most readily available constituents of the oceans, rather than more esoteric messenger molecules that might be capable of more refined function but would need to be specifically synthesized.

For cell membranes, there is another advantage in organization that is based on the hydrophobic effect. The "seal" that holds the membrane together – hydrocarbon chains of the lipids, hydrophobic side chains of proteins – is a *liquid* seal. It allows the cell to be deformed, squeezed by contact with other cells, etc., without disruption of the containment wall that holds the cell contents together. The normal presence on membrane lipids of a saturated and unsaturated hydrocarbon chain on the same lipid molecule (figure 1) has undoubtedly developed for the same reason – to prevent crystallization of the membrane interior at cold temperatures.

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On the role of water in molecular recognition and self-assembly

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Abstract. The conventional concept of hydrophobic interaction is generalized to include any kind of solvent-induced effects on the binding of two or more solutes in aqueous solutions. Specifically, we focus on the role of hydrogen-bonding between the solutes and solvent molecules. A qualitative examination of the solute-solvent hydrogen-bonding effect on molecular recognition, self-assembly, and stabilization of biopolymers shows that these effects might be quite large and possibly more important than direct interactions between solute particles.

Keywords. Molecular recognition; self-assembly; role of water; solvent-induced effects; hydrophobic interaction.

1. Introduction

The importance of the presence of water in biological processes has long been recognized. However, very little quantitative work has been done to elucidate the role of water in these processes. One concept that has emerged from these studies is the concept of hydrophobic interaction (HI) (Kauzmann 1959; Tanford 1973; Ben-Naim 1980). In its most primitive sense, this concept was coined to describe the tendency of nonpolar molecules, or nonpolar side-chain groups on biomolecules, to adhere to each other, thereby minimizing their exposure to the solvent. The concept itself, although far from being understood on a molecular level, has been applied to many complex processes, such as binding of substrate to enzymes, association of subunits to form multisubunit enzymes, association of proteins to DNA, self-assembly of macromolecules, and even to interaction between entire cells. Clearly, these processes involve many factors in addition to the so-called HI, such as hydrogen-bonds (HB) and electrostatic interactions. Some of these originate from the interacting particles themselves, and others have their origin in the solvent. We shall, therefore, start in §2 with an exact separation of the two sets of factors. Next, we shall focus on the solvent-induced factors; these will also be separated into what we may call the conventional and nonconventional HI. This is described in §3. In §4 we further classify the various contributions to the HI according to the various functional groups (FG) and according to their location on the surface of the biomolecules.

In §5 we define the concept of molecular recognition, and in §6 we make one numerical estimate of the solvent-induced contribution to this process. Two possible extensions of the study of solvent effect, the self-assembly and protein folding, are briefly discussed in §§7 and 8.

2. Hydrophobic interactions and binding thermodynamics

The concept of HI has been used in the literature to describe various phenomena. Kauzmann coined the term hydrophobic bond to describe the tendency of nonpolar solutes (or of side-chain groups on a protein) to adhere to each other in aqueous media (Kauzmann 1959; Ben-Naim 1980). This term has evolved into HI and is currently used to describe the binding tendency of two or more nonpolar solutes in water.

A fundamentally different process, which is also included under the concept of HI or the hydrophobic effect (Tanford 1973), is the transfer of a nonpolar solute from a nonaqueous into aqueous solvent. The latter is more recently referred to as hydrophobic solvation (Ben-Naim 1980). Némethy and Scheraga (1962) argued that the formation of dimers by nonpolar solutes can be viewed as a partial reversal of the process of hydrophobic solvation and, therefore, the thermodynamics of the two concepts; HI and hydrophobic solvation should be simply related to each other. A close analysis of the thermodynamics of these two processes reveals that such a relationship does exist only in very special cases (Ben-Naim 1980) (e.g., the formation of a "dimer" at zero separation or aggregation of a very large number of solute particles to form a compact droplet in aqueous solutions).

Perhaps the simplest experimental model that has been used to study HI is the dimerization of a series of carboxylic acids in various solvents.

Schrier *et al* (1964) proposed a method of extracting information on HI from the standard free energy of dimerization of carboxylic acids, which we denote by $\Delta G_B^0(R_n \text{ COOH})$, where R_n is the alkyl chain with n carbon atoms.

Assuming that for each carboxylic acid one can write:

$$\Delta G_B^0 = \Delta G_{\text{HI}}^0 + \Delta G_{\text{HB}}^0, \quad (1)$$

where ΔG_{HI}^0 is the contribution due to HI, and ΔG_{HB}^0 is the contribution due to hydrogen-bonding. Furthermore, assuming that ΔG_{HB}^0 is common to all the carboxylic acids, and in particular, in the case of formic acid where we have only HB, i.e.,

$$\Delta G_B^0(\text{H COOH}) = \Delta G_{\text{HB}}^0, \quad (2)$$

One can extract information on the HI from ΔG_B^0 by subtracting the HB contribution, i.e.:

$$\Delta G_{\text{HI}}^0(R_n \text{ COOH}) = \Delta G_B^0(R_n \text{ COOH}) - \Delta G_B^0(\text{H COOH}). \quad (3)$$

However, a close examination of the content of the free energy of dimerization shows that theory does not support the above procedure (Ben-Naim 1980).

The standard free energy of dimerization (based on the molar concentration scale) may be written as

$$\Delta G_B^0 = \Delta U_B + \delta G + kT \ln(q_M^2/q_D), \quad (4)$$

where ΔU_B is the direct binding energy between the two monomers, δG is the indirect or solvent-induced contribution to the binding free energy, and the last term on the right-hand side (RHS) of (4) contains the momentum and the rotational-vibrational partition functions of the monomers (M) and the dimer (D).

Clearly, even without any further analysis of the quantity δG (which we shall carry out in the next section), the form of ΔG_B^0 in (4) does not suggest a split of the form (1) into two contributions.

In 1971, a new definition of HI was suggested (Ben-Naim 1971, 1980). Recognizing the almost universal application of this concept to nonpolar solutes in aqueous solutions, it was argued that one should focus on δG as being a measure of the HI. The two other terms in (4) are presumed to be (approximately) invariant to changes of the solvent. Taking the extreme case of an ideal gas (i.g.) in which the same dimerization process is carried out, we find that:

$$\Delta G_B^{0,\text{i.g.}} = \Delta U_B + kT \ln (q_M^2/q_D), \quad (5)$$

i.e., in the ideal gas phase, $\delta G = 0$. Hence, from (4) and (5), one can extract the solvent-induced contribution, namely:

$$\delta G = \Delta G_B^0 - \Delta G_B^{0,\text{i.g.}}. \quad (6)$$

The general split of ΔG_B^0 in (4) is useful, since it does separate the driving force for binding into three factors. One depends on the direct interaction between the two monomers. This could include any type of direct interaction, such as van der Waal, HB, or electrostatic interaction. The third term on the RHS of (4) includes properties of the monomers and dimers, such as the mass, moment of inertia, vibrational frequencies etc. Both of these terms depend *only* on properties of the monomers and the dimers. In contrast, the quantity δG is a statistical mechanical quantity and involves averages over all configurations of the solvent molecules. This is essentially a many-body-interaction quantity, depending on the properties of the solvent and on the solute-solvent interaction. This feature of δG makes it more difficult to study by theoretical means.

For two simple solutes such as methane in water, an approximate measure of δG in terms of experimental quantities has been suggested (Ben-Naim 1971, 1980), namely,

$$\delta G = \Delta G_{\text{ethane}}^* - 2\Delta G_{\text{methane}}^*, \quad (7)$$

where on the RHS of (7) we have the solvation free energies of ethane and methane (Ben-Naim 1987). This quantity has been found useful and convenient for comparing various liquids as solvents.

Originally, the quantity δG has been suggested as a measure of HI in the conventional sense, i.e., for the indirect or solvent-induced part of the interaction between two *nonpolar* solutes in aqueous solutions. However, the significance of δG , as a solvent-induced contribution to ΔG_B^0 , is retained even when the binding solutes are not simple nonpolar particles, e.g., carboxylic acids, as discussed above, or proteins, as we shall discuss in subsequent sections.

Clearly, in the case of carboxylic acids, the conventional HI may be applied to describe the interaction between the nonpolar alkyl groups, as was suggested by Schrier *et al* (1964). However, since the entire molecules are certainly not nonpolar, we could not have used the term HI, in its conventional sense, to apply to the entire solvent-induced quantity δG as defined in (6).

Fortunately, the split of ΔG_B^0 in (4) holds true for any binding process (assuming that classical statistical mechanics can be applied to our systems). Therefore, we shall generalize the concept of HI to include any type of solvent-induced

contribution to ΔG_B^0 . We shall thus use the concept of HI in a nonconventional sense when it is applied to complex solutes. It will coincide with the conventional sense of HI when our solutes are simple nonpolar. The exact formalism that makes this generalization is discussed in the next section.

3. Formal split of δG into conventional and nonconventional HI

Consider two solutes, say a protein P and a ligand L, at infinite dilution in water. In §2 we wrote the standard free energy of binding ΔG_B^0 as comprising three terms [see (4)]. We shall now focus on the solvent-induced quantity δG , which may be written as (Ben-Naim 1980):

$$\delta G = -kT \ln \left\{ \frac{\langle \exp[-\beta B_{PL}] \rangle_0}{\langle \exp[-\beta B_P] \rangle_0 \langle \exp[-\beta B_L] \rangle_0} \right\}. \quad (8)$$

Here, $\beta = (kT)^{-1}$ with k the Boltzmann constant and T the absolute temperature. B_α is referred to as the total binding energy of α to the solvent, i.e.,

$$B_\alpha = \sum_{i=1}^N U(\mathbf{X}_\alpha, \mathbf{X}_i), \quad (9)$$

where $U(\mathbf{X}_\alpha, \mathbf{X}_i)$ is the pair potential function for the interaction between the solute α and the i th water molecule, the pair being at a specific configuration, denoted by $(\mathbf{X}_\alpha, \mathbf{X}_i)$. The symbol $\langle \rangle_0$ denotes an average over all configurations of the solvent molecules in the TPN ensemble. In what follows, we shall use, for notational simplicity, the T, V, N ensemble. One can show that the difference between the Helmholtz and the Gibbs free energies is quite negligible for the processes discussed in this article (Ben-Naim 1987).

We also assume for simplicity that the solutes P, L and the complex PL are rigid molecules. Normally one should allow for some conformational flexibility of the molecule, in which case an additional average over all possible conformations must be carried out in (8) (Ben-Naim 1980, 1987).

The quantity δG may be interpreted as the indirect (or solvent-induced) part of the free energy change for the process of bringing P and L from fixed configuration at infinite separation to a fixed configuration at the final state of the complex, which we denote by PL.

Each of the average quantities in (8) has the form,

$$\langle \exp[-\beta B_\alpha] \rangle_0 = \int d\mathbf{X}^N \exp[-\beta B_\alpha] P_0(\mathbf{X}^N), \quad (10)$$

where $P_0(\mathbf{X}^N)$ is the probability distribution function for finding a configuration $\mathbf{X}^N = \mathbf{X}_1 \dots \mathbf{X}_N$ of all the solvent molecules in the *absence* of the solutes (i.e., in the pure solvent, hence the subscript 0 used in the notation $\langle \rangle_0$). More explicitly,

$$P_0(\mathbf{X}^N) = \{\exp[-\beta U_N(\mathbf{X}^N)]\} / \{\int d\mathbf{X} \exp[-\beta U_N(\mathbf{X}^N)]\}. \quad (11)$$

In what follows, we assume that for each of the solute-solvent pair potentials we can write

$$U(\mathbf{X}_\alpha, \mathbf{X}_i) = U^H(\mathbf{X}_\alpha, \mathbf{X}_i) + U^F(\mathbf{X}_\alpha, \mathbf{X}_i), \quad (12)$$

where U^H is the hard-core interaction, i.e., the steep repulsive interaction between α and the i th water molecule at a very short distance. The second term U^F includes all other interactions between α and a water molecule, such as van der Waals, hydrogen-bond, and electrostatic. These arise from functional groups (FG) on the surface of α (by surface, we mean any region of α which is exposed to the solvent).

For some specific applications, we may further split U^F into a van der Waals term and a specific term due to, say, HB or electrostatic interactions, i.e.,

$$U^F(\mathbf{X}_\alpha, \mathbf{X}_i) = U^S(\mathbf{X}_\alpha, \mathbf{X}_i) + U^{HB}(\mathbf{X}_\alpha, \mathbf{X}_i) + \dots \quad (13)$$

Corresponding to this split of the pair potential, we have for the total binding energy of each solute α ,

$$B_\alpha = B_\alpha^H + B_\alpha^S + B_\alpha^{HB} + \dots \quad (14)$$

From now on, we shall assume that the surface of the solute contains either nonpolar FG (such as methyl, ethyl etc.) or FG that form HB (such as hydroxyl, amine etc). We shall not discuss the case of charged FG (such as ionized carboxyl or ammonium groups). Also, to simplify the notation, we combine B_α^H and B_α^S into one term B_α^{HS} and rewrite B_α simply,

$$B_\alpha = B_\alpha^{HS} + B_\alpha^{HB}. \quad (15)$$

Using (15) in each of the average quantities in (8) induces a factorization of each average term as follows,

$$\begin{aligned} \langle \exp[-\beta B_\alpha] \rangle_0 &= \int d\mathbf{X}^N \exp[-\beta B_\alpha^{HS} - \beta B_\alpha^{HB}] P_0(\mathbf{X}^N) \\ &= \frac{\int d\mathbf{X}^N \exp[-\beta U_N - \beta B_\alpha^{HS} - \beta B_\alpha^{HB}] \int d\mathbf{X}^N \exp[-\beta U_N - \beta B_\alpha^{HS}]}{\int d\mathbf{X}^N \exp[-\beta U_N - \beta B_\alpha^{HS}] \int d\mathbf{X}^N \exp[-\beta U_N]} \\ &= \langle \exp[-\beta B_\alpha^{HB}] \rangle_{HS} \langle \exp[-\beta B_\alpha^{HS}] \rangle_0, \end{aligned} \quad (16)$$

where the symbol $\langle \rangle_{HS}$ signifies a *conditional* average, i.e., this is an average over all configurations of the solvent molecules, given that the hard (H) and soft (S) parts of the potential have been "turned on." This average employs the conditional distribution function,

$$P_{HS}(\mathbf{X}^N/\mathbf{X}_\alpha) = \{\exp[-\beta U_N - \beta B_\alpha^{HS}]\} / \{\int d\mathbf{X}^N \exp[-\beta U_N - \beta B_\alpha^{HS}]\}, \quad (17)$$

which is the probability density of finding a configuration $\mathbf{X}^N$, given that the hard and soft part of B_α have been "turned on" at some specific configuration $\mathbf{X}_\alpha$.

The factorization (16) has a simple interpretation in terms of the solvation free energy of the solute α (Ben-Naim 1967), i.e.,

$$\begin{aligned} \Delta G_\alpha^* &= -kT \ln \langle \exp[-\beta B_\alpha] \rangle_0 = -kT \ln \langle \exp[-\beta B_\alpha^{HS}] \rangle_0 \\ &\quad - kT \ln \langle \exp[-\beta B_\alpha^{HB}] \rangle_{HS} = \Delta G_\alpha^{*HS} + \Delta G_\alpha^{HB/HS}, \end{aligned} \quad (18)$$

where ΔG_α^{*HS} is the solvation free energy of the hard and soft parts of the

solute-solvent interaction, and $\Delta G_{\alpha}^{*HB/HS}$ is the *conditional* solvation free energy of the HB part, given that the hard and soft parts have already been solvated.

Using the factorization (16) for each of the average quantities in (8), one can write δG as,

$$\delta G = \delta G^{HS} + \delta G^{HB/HS}, \quad (19)$$

where

$$\delta G^{HS} = -kT \ln \left\{ \frac{\langle \exp[-\beta B_{PL}^{HS}] \rangle_0}{\langle \exp[-\beta B_P^{HS}] \rangle_0 \langle \exp[-\beta B_L^{HS}] \rangle_0} \right\}, \quad (20)$$

and
$$\delta G^{HB/HS} = -kT \ln \left\{ \frac{\langle \exp[-\beta B_{PL}^{HB}] \rangle_{HS}}{\langle \exp[-\beta B_P^{HB}] \rangle_{HS} \langle \exp[-\beta B_L^{HB}] \rangle_{HS}} \right\}, \quad (21)$$

Thus, δG^{HS} is the solvent-induced contribution to δG that arises only from the hard and soft (HS) parts of the solute-solvent interactions. The HB (or also charged groups, if they exist) are presumed to be "turned off." This part may be referred to as the *conventional* HI, since it is applied to two nonpolar solutes in water. The second term $\delta G^{HB/HS}$ is the contribution due to turning on the HB part of the interaction. This is still a solvent-induced contribution to δG and may be referred to as a *nonconventional* HI. It is nonconventional only in the traditional usage of the term HI, but as we stressed above, it is well within the general definition of HI in terms of δG (Ben-Naim 1971, 1980).

Perhaps we should point out that the term HI, in the traditional sense, has been applied to hydrophobic solutes, i.e., solutes with relatively low solubility in water. The generalized concept of HI, as defined above in terms of δG , include also the case of very hydrophilic solutes, such as polyalcohols or hydrophilic proteins. Although we shall find in the next sections that these solutes could be effectively attracted to each other in aqueous solutions, such an attraction cannot conceptually be attributed to "phobia" toward water.

Clearly, for some specific applications, one may choose to split B_{α} in different ways, e.g., to separate the hard and soft part or to add an electrostatic part to the solute-solvent interaction. The formalism developed above can be adapted with minor notational modification only.

4. Classification of regions on the surface of the solutes

In the previous section, we have examined the formal split of δG into a conventional and nonconventional HI. In order to proceed with the examination of the different contributions to δG , it is convenient to distinguish between three different regions on the polymers.

Letting α be either P or L, we assume that α is a large protein or nucleic acid. We also assume that the solute-solvent pair potential may be written as,

$$U(\mathbf{X}_{\alpha}, \mathbf{X}_i) = U^H(\mathbf{X}_{\alpha}, \mathbf{X}_i) + \sum_{k=1}^M U^F(\mathbf{X}_k, \mathbf{X}_i), \quad (22)$$

where $U^H(\mathbf{X}_{\alpha}, \mathbf{X}_i)$ is the hard-core repulsive interaction between the solute α and the i th water molecule. $U^F(\mathbf{X}_k, \mathbf{X}_i)$ is the interaction between the k th functional

group on the surface of α and the i th water molecule. This function may include van der Waals, charge-charge, HB etc., interactions. The main distinction between the two terms of the RHS of (22) is that, while U^H depends on the entire solute α , the second part U^F depends only on groups that are in contact with the water, and by definition, these groups belong to the surface of α .

The binding energy of α to the solvent can be written as,

$$B_\alpha = \sum_{i=1}^N U(\mathbf{X}_\alpha, \mathbf{X}_i) = B_\alpha^H + \sum_{k=1}^M B_{\alpha,k}^F, \quad (23)$$

where $B_{\alpha,k}^F$ is the total binding energy of the k th FG on the surface of α (excluding the hard-core repulsive interaction).

Using a similar procedure as in §3, we can write the solvation free energy of α as,

$$\begin{aligned} \Delta G_\alpha^* &= -kT \ln \langle \exp[-\beta B_\alpha] \rangle_0 \\ &= -kT \ln \left\{ \langle \exp[-\beta B_\alpha^H] \rangle_0 \left\langle \exp \left[-\beta \sum_{k=1}^M B_{\alpha,k}^F \right] \right\rangle_H \right\} \\ &= \Delta G_\alpha^{*H} + \Delta G_\alpha^{*F/H}, \end{aligned} \quad (24)$$

where ΔG_α^{*H} is the solvation free energy of the hard-core part of the interaction (essentially the work required to create a cavity in the solvent), and $\Delta G_\alpha^{*F/H}$ is the conditional solvation free energy of all the FG on the surface of α , given that the hard part of the interaction is already "turned on." This quantity depends on the entire volume of α through the condition "H" which essentially excludes the water molecules from the excluded volume of α with respect to the solvent. On the other hand, the quantity $B_{\alpha,k}^F$ depends only on the constituency of the surface of α , i.e. on the FG that are in direct contact with the solvent. This separation is useful for the classification of the various sources of contributions to δG as discussed below.

We now classify all the FG on the surface of either P or L into three groups (see figure 1):

- (1) The region E (for external) includes all FG which are not affected by the binding of P and L to form the complex PL. Intuitively, any FG that is far away from the binding region between P and L will not "notice" the occurrence of the binding (in a sense discussed below).
- (2) The region I (for inner) includes all FG on either P or L which contribute to $\Delta G_P^{*F/H}$ and to $\Delta G_L^{*F/H}$ but not to $\Delta G_{PL}^{*F/H}$. Intuitively, these FG are exposed to the solvent when P and L are separated but are not exposed to the solvent in the complex PL.
- (3) The third region J (for joint) includes all FG that are neither in E nor in I. These are the FGs that are exposed to the solvent before and after the binding, but the extent of solvation might be different in the two states of the solutes P and L.

We now make the requirements for the classification of the FG more precise. First, for each of the solutes P and L, we write,

$$\begin{aligned} \langle \exp[-\beta B_{P,E}^F - \beta B_{P,I}^F - \beta B_{P,J}^F] \rangle_H &= \langle \exp[-\beta B_{P,J}^F] \rangle_H \times \\ &\quad \langle \exp[-\beta B_{P,E}^F - \beta B_{P,I}^F] \rangle_{H,P,I} \end{aligned}$$

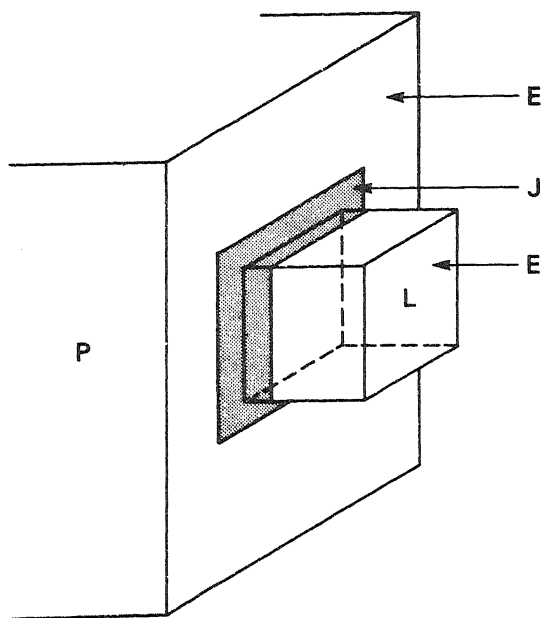


Figure 1. The three regions, E, I, and J, on the two solutes P and L.

$$= \langle \exp[-\beta B_{P,J}^F] \rangle_H \langle \exp[-\beta B_{P,E}^F] \rangle_{H,P} \langle \exp[-\beta B_{P,I}^F] \rangle_{H,P}, \quad (25)$$

and similarly

$$\begin{aligned} \langle \exp[-\beta B_{L,E}^F - \beta B_{L,I}^F - \beta B_{L,J}^F] \rangle_H &= \langle \exp[-\beta B_{L,J}^F] \rangle_H \times \\ &\quad \langle \exp[-\beta B_{L,E}^F - \beta B_{L,I}^F] \rangle_{H,L}, \\ &= \langle \exp[-\beta B_{L,J}^F] \rangle_H \langle \exp[-\beta B_{L,E}^F] \rangle_{H,L} \langle \exp[-\beta B_{L,I}^F] \rangle_{H,L}. \end{aligned} \quad (26)$$

In (25) and (26) we first write B_α^F as a sum of three contributions due to the FG in regions E, I, and J. Next, we transform it into a product of two conditional averages, as we have done in §3. Note that the conditions P_J or L_J means that the interaction due to FG in the J region (of P or L) are turned on. Finally, we assume that the regions E and I are independent, which leads to a factorization of the average over the product of $\exp[-\beta B_{\alpha,E}^F] \exp[-\beta B_{\alpha,I}^F]$ into a product of two averages.

Similarly, for the PL complex, we write,

$$\begin{aligned} \langle \exp[-\beta B_{PL,E}^F - \beta B_{PL,J}^F] \rangle_H &= \langle \exp[-\beta B_{PL,J}^F] \rangle_H \times \\ &\quad \langle \exp[-\beta B_{P,E}^F - \beta B_{L,E}^F] \rangle_{H,P,J,L} \\ &= \langle \exp[-\beta B_{PL,J}^F] \rangle_H \langle \exp[-\beta B_{P,E}^F] \rangle_{H,P,J,L} \times \\ &\quad \langle \exp[-\beta B_{L,E}^F] \rangle_{H,P,J,L}. \end{aligned} \quad (27)$$

In the PL complex, by definition, there is no contribution from the region I to B_{PL}^F . We again transformed into conditional averages and assume that the E region on P and the E region on L are independent.

We can now combine (25), (26), and (27) and rewrite (8) as follows [note (24)],

$$\begin{aligned}\delta G &= \delta G^H + \delta G^{F/H} = [\Delta G_{PL}^{*H} - \Delta G_P^{*H} - \Delta G_L^{*H}] \\ &\quad - kT \ln \langle \exp[-\beta B_{PL,J}^F] \rangle_H \\ &\quad + kT \ln \langle \exp[-\beta B_{P,I}^F - \beta B_{P,J}^F] \rangle_H \langle \exp[-\beta B_{L,I}^F - \beta B_{L,J}^F] \rangle_H,\end{aligned}\quad (28)$$

where all the contributions due to region E are cancelled out. [Note that the conditions P_J in (25) and L_J in (26) are slightly different from the condition $P_J L_J$ in (27), but we ignore this difference in cancelling the terms that include contributions from region E].

In (28) we have three distinctly different contributions to the solvent-induced quantity δG . The first is due to the change in the "cavities" of P and L upon the formation of the complex PL. This term will always be positive, since the excluded volume of PL is always smaller than the excluded volume of P and L separately. The second term on the RHS of (28) is the "gain" of solvation in the J region due to the binding. The third term is due to the "loss" of solvation of regions I and J of the separate solutes P and L.

If we can assume that the regions I and J are independent (or weakly dependent), we can rewrite (28) in a somewhat more convenient form, i.e.,

$$\begin{aligned}\delta G &= \delta G^H - kT \ln \left\{ \frac{\langle \exp[-\beta B_{PL,J}^F] \rangle_H}{\langle \exp[-\beta B_{P,J}^F] \rangle_H \langle \exp[-\beta B_{L,J}^F] \rangle_H} \right\} \\ &\quad + kT \ln \langle \exp[-\beta B_{P,I}^F] \rangle_H \langle \exp[-\beta B_{L,I}^F] \rangle_H.\end{aligned}\quad (29)$$

In this form, the last term contains only the "loss" of solvation of the region I, whereas the second term has the form of a correlation function. It measures the extent of dependence between FG in the region J on P and L in the state PL relative to the state when P and L are separated (and hence independent). We can rewrite (29) in a shorthand notation as follows,

$$\delta G = \delta G^H + \delta G_J^{F/H} + \delta G_I^{F/H}, \quad (30)$$

where each term on the RHS of (30) denotes the corresponding terms on the RHS of (29).

5. The various contributions to molecular recognition

The concept of molecular recognition is usually discussed in terms of the so-called "key and lock" model (figure 2). This is essentially equivalent to the statement that the direct binding energy ΔU_B to a particular site A (which is the one to be recognized) is minimal with respect to all other possible binding sites i , i.e.

$$\Delta U_B(A) = \min \Delta U_B(i). \quad (31)$$

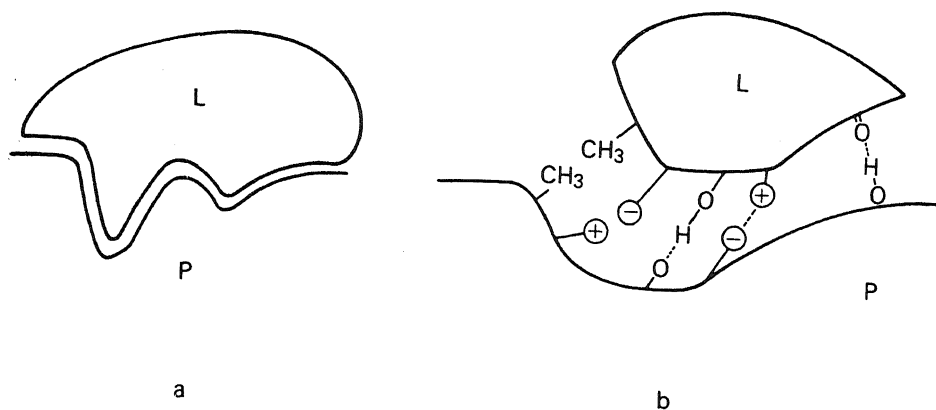


Figure 2. (a) The classical "lock and key" model. Here, the geometrical fit maximizes the van der Waals interaction between P and L. (b) Various possible contributions to the direct interaction between P and L, such as van der Waals, hydrogen bonds, and electrostatic interactions.

Clearly, this statement is valid as a criterion for recognition if the binding process takes place in a vacuum. An interesting model for molecular recognition based on direct interactions has been presented by Stillinger and Wasserman (1978).

However, in a solvent the recognition criterion (31) should be replaced by

$$\Delta G_B(A) = \min_i \Delta G_B(i) = \min_i [\Delta U_B(i) + \delta G(i)], \quad (32)$$

where $\Delta G_B(i)$ is the sum of the direct and indirect parts of the binding free energy at the site i^* .

The indirect part has been split into three terms [(30)]:

$$\delta G = \delta G^H + \delta G_I^{F/H} + \delta G_I^{F/H} \quad (33)$$

Each of the terms in (32) and (33) can contribute to the specificity of the molecular recognition. The simplest to visualize is clearly the role of ΔU_B . The strongest interaction between P and L at a particular site would lead to recognition. This can be achieved either through the "key and lock" mechanism or by a specific pattern of hydrogen-bonding FG on P and L. Both of these effects can operate simultaneously to minimize ΔU_B . The various contributions to δG are more subtle. δG^H depends essentially on the change of the excluded volumes of P and L upon the formation of the complex. Since binding will always reduce the excluded volume of P and L, δG^H is always negative and tends to enhance the association. This effect is similar to the "key and lock" mechanism. The tighter the binding between L and P, the larger is the reduction in the excluded volume and the larger the contribution to δG^H . In contrast to ΔU_B , the term δG^H depends only on the overlapping of the excluded volumes of P and L but is independent of the type of the FG in the I regions of P and L.

* In this article we assume that the concept of recognition is an equilibrium concept, i.e., the binding partners find each other under equilibrium conditions. It is, in principle, possible that kinetic effects other than, and independent of, $\Delta G_B(i)$ will contribute to the recognition under nonequilibrium conditions (Yi-der Chen and Ben-Naim 1987).

The quantity $\delta G_1^{F/H}$ is due to the loss of the solvation free energy of the FG in the region I of P and L. It is clear from (29) that the larger the binding energy of these FG to the solvent, the larger will be the tendency for dissociation. From the point of view of recognition, the site which will be most favoured for binding is the site that provides the weakest binding energy to the solvent. Qualitatively, this effect is in conformity with the experimental observation that binding sites are often characterized by being "hydrophobic," meaning that they are dominated by nonpolar FG, hence providing relatively weak interaction with the solvent.

Perhaps the most subtle and potentially important contribution to δG is contained in $\delta G_J^{F/H}$. This term depends on the correlation between FG in the J region when P and L form the complex PL. One of the characteristic features of this quantity is that, if we have two FG – one on P and the other on L – which can be connected by a chain of water molecules through HB, then we should obtain a large negative contribution to δG . This is quite unique to liquid water because of the ability of a water molecule to form simultaneous HB with two FG on P and L. This contribution is highly specific in the sense that its value will strongly depend on the locations and orientations of these FG. In the next section we shall discuss some quantitative aspects of this particular effect on δG . In another paper, we have also suggested an experimental way of studying this effect by using small model-compound molecules (Ben-Naim *et al* 1987).

6. Estimates of the contribution of hydrogen bonding in the J region to molecular recognition

In §§4 and 5 we identified three different contributions to δG , each of which can be specific in the sense of contributing to the recognition of a particular binding site. In this and in the following sections, we shall focus on one of these contributions, namely $\delta G_J^{F/H}$, which we believe is the most sensitive to subtle changes in the locational and orientational distribution of FG. Furthermore, we also restrict ourselves to FG that can form HB with solvent molecules.

With these restrictions in mind, we rewrite the term $\delta G_J^{F/H}$ from (30) in the modified form,

$$\delta G_J^{HB/H} = -kT \ln \left\{ \frac{\langle \exp[-\beta B_{PL}^{HB}] \rangle_H}{(\langle \exp[-\beta B_P^{HB}] \rangle_H \langle \exp[-\beta B_L^{HB}] \rangle_H)} \right\}, \quad (34)$$

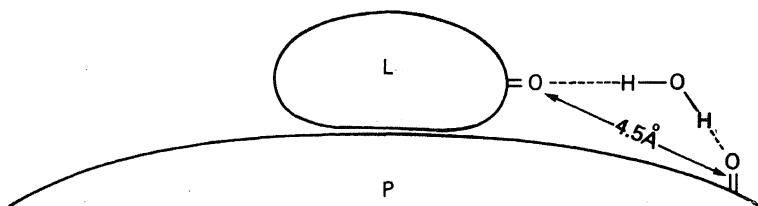


Figure 3. Two carbonyl groups, one in the J region of P and the second in the J region of L, at a distance of 4.5 Å. The orientations of these two groups is such that they can form a bridge by means of HB to one water molecule.

where F is replaced by the superscript HB. For notational simplicity we also omit the subscript J on the RHS of (34).

We further assume that in the bound state PL, the J region contains pairs of FG, say hydroxyl or carbonyl groups, one on P and one on L, and that they are at a distance close to 4.5 Å and oriented in such a way that they can form simultaneous HB with a single water molecule (figure 3).

Furthermore, if there are N_{PL}^{HB} such pairs of FG in this region, they are presumed to be far apart so that they can be treated as independent (figure 4).

We now write the total binding energy B_{PL}^{HB} as:

$$B_{PL}^{HB} = \sum_{l=1}^{N_{PL}^{HB}} B_l^{HB}, \quad (35)$$

where

$$B_l^{HB} = \sum_{i=1}^N U_i^{HB}(\mathbf{X}_{PL}, \mathbf{X}_i). \quad (36)$$

Here, B_l^{HB} is the binding energy through HB of the l th pair of FG (in the J region), and U_i^{HB} is the HB part of the interaction between the l th pair and the i th water molecule at the specified configuration $(\mathbf{X}_{PL}, \mathbf{X}_i)$.

Following the assumption of independence of the pairs of FGs, each of the average quantities in (34) may be factored into N_{PL}^{HB} factors; thus, we obtain:

$$\delta G_J^{HB/H} = -kTN_{PL}^{HB} \ln \left\{ \frac{\langle \exp[-\beta B_{PL,l}^{HB}] \rangle_H}{\langle \exp[-\beta B_{P,l}^{HB}] \rangle_H \langle \exp[-\beta B_{L,l}^{HB}] \rangle_H} \right\}, \quad (37)$$

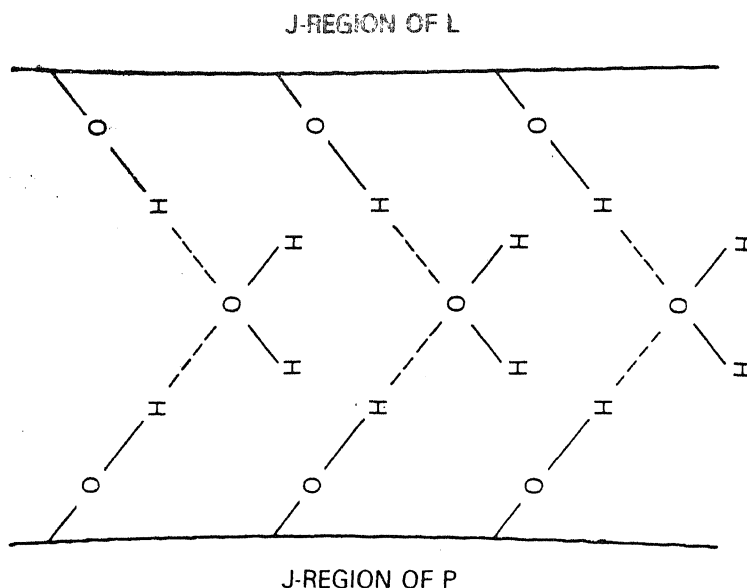


Figure 4. Pairs of FG along the J regions of P and L each of which can form a hydrogen-bonded bridge with one water molecule. The pairs are presumed to be far apart so that they act independently.

where we assume, for simplicity, that all FG have the same binding energy to the solvent; therefore, instead of summing over all kinds of FG, we simply take N_{PL}^{HB} identical terms in (37).

We now wish to estimate the contribution to $\delta G_J^{HB/H}$ from each of the pairs of FG in the J region. Since the pair of FG is oriented as described in figure 3, only *one* water molecule can interact with this pair, either by forming one or two HB with this pair. Therefore, the entire range of configurations of the solvent molecule may be split as follows:

$$\int \exp[-\beta B_{PL,l}^{HB}] P(\mathbf{X}^N/\mathbf{X}_{PL}^H) d\mathbf{X}^N =$$

$$\sum_{i=1}^N \int \exp[-\beta U_l^{HB}(\mathbf{X}_{PL}, \mathbf{X}_i)] P(\mathbf{X}^N/\mathbf{X}_{PL}^H) d\mathbf{X}^N$$

ith water molecule
hydrogen-bonded to l

$$+ \int P(\mathbf{X}^N/\mathbf{X}_{PL}^H) d\mathbf{X}^N. \quad (38)$$

no hydrogen bonds to l

The first term on the RHS of (38) includes all configurations of the solvent molecules, for which one water molecule is hydrogen bonded to the *l*th pair of FG. Since only one water molecule can form such HB with the *l*th pair, one can simply rewrite this as *N* times an integral for which one *specific* water molecule, say *i* = 1, is hydrogen bonded to this pair. This integral can be further split into three integrals as follows:

$$\int \text{water 1 hydrogen bonded to } l = \int \text{water 1 hydrogen bonded to P only} + \int \text{water 1 hydrogen bonded to L only} + \int \text{water 1 hydrogen bonded to both P and L} \quad (39)$$

where the three terms on the RHS of (39) correspond to the three cases for which water number 1 is hydrogen bonded to either P, L, or to both P and L, respectively.

The second term on the RHS of (38) includes all configurations for which no water molecule is hydrogen bonded to the *l*th pair of FG. This may be written as*:

$$\int P(\mathbf{X}^N/\mathbf{X}_{PL}^H) d\mathbf{X}^N = 1 - N \int \dots - N \int \dots - N \int \dots \quad (40)$$

no HB to l water 1 hydrogen bonded to P only water 1 hydrogen bonded to L only water 1 hydrogen bonded to both P and L

Combining (38) and (40), we have:

* "... means the same integrand as in the preceding integral.

$$\int \exp[-\beta B_{PL,l}^{HB}] P(\mathbf{X}^N/\mathbf{X}_{PL}^H) d\mathbf{X}^N = 1 + N \int \{\exp[-\beta U_l^{HB}] - 1\} P(\mathbf{X}^N/\mathbf{X}_{PL}^H) d\mathbf{X}^N$$

water 1
hydrogen
bonded to P only

$$+ N \int \dots + N \int \dots \quad (41)$$

water 1
hydrogen
bonded to L only

water 1
hydrogen
bonded to both P and L

Since the range of configurations of a water molecule allowable for the formation of HB is very restricted, we can approximate each of the integrals on the RHS of (41) as follows:

$$N \int \{\exp[-\beta U_l^{HB}] - 1\} d\mathbf{X}_1 \int P(\mathbf{X}^N/\mathbf{X}_{PL}^H) d\mathbf{X}^{N-1}$$

water 1
hydrogen
bonded to P only

all
configurations

$$= \int \{\exp[-\beta U_l^{HB}] - 1\} \rho(\mathbf{X}_1/\mathbf{X}_{PL}^H) d\mathbf{X}_1 \approx [\exp(10) - 1] \rho_w (\eta - \eta').$$

water 1
hydrogen
bonded to P only

(42)

On the last step on the RHS of (42), we have made the following approximations. Since the region of integration for which the integrand is nonzero is presumed to be small, we replaced the integral by a product of the value of the integrand at some point within the region of integration times the volume of this region. In this region $-\beta U_l^{HB} \approx 10$ (for hydrogen bond energy at room temperature). The conditional density $\rho(\mathbf{X}_1/\mathbf{X}_{PL}^H)$ is replaced by the density of water at room temperature ρ_w . η is the volume of the region for which a water molecule can form a HB with one FG. From this we subtract η' , the volume of the region for which a water molecule can form two HB with the two FG. See appendix A for estimates of η and η' . Applying similar approximations to each of the integrals in (41), we can write the entire average quantity in the numerator of (37) as:

$$\langle \exp[-\beta B_{PL,l}^{HB}] \rangle_H = 1 + 2\rho_w (\eta - \eta') [\exp(10) - 1] + \rho_w \eta' [\exp(20) - 1]. \quad (43)$$

Similarly, for each of the average quantities in the denominator of (37), we write the approximation:

$$\langle \exp[-\beta B_{P,l}^{HB}] \rangle_H \approx \langle \exp[-\beta B_{L,l}^{HB}] \rangle_H \approx 1 + \rho_w \eta [\exp(10) - 1]. \quad (44)$$

Note that in (44) we have the full range of configurations for which a water

molecule can form a HB with *one* FG. This is denoted by η . On the other hand, in (42) we put $\eta - \eta'$ to take into account the reduction of this range of configurations when a second FG is present. For more details, see appendix A.

Thus, for the entire quantity in (37), we have the approximation:

$$\delta G_J^{\text{HB/H}} = -kTN_{\text{PL}}^{\text{HB}} \ln \left\{ \frac{1 + 2\rho_w(\eta - \eta') \exp(10) + \rho_w\eta' \exp(10)}{1 + 2\rho_w\eta \exp(10) + (\rho_w\eta)^2 \exp(20)} \right\}. \quad (45)$$

Taking the density of water at room temperature as $\rho_w = 5.5 \times 10^{-2} \text{ mol cm}^{-3}$ and using the estimates of $\eta = 5.74 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ and $\eta' = 20/360 \eta$ from appendix A, we may estimate the entire quantity $\delta G_J^{\text{HB/H}}$ per pair of FG as:

$$\delta G_J^{\text{HB/H}}/N_{\text{PL}}^{\text{HB}} = -3.37 \text{ kcal/mol}. \quad (46)$$

Although this is a very crude estimate, it does indicate that the solvent-induced effect through hydrogen bonding might be of an order of magnitude similar to the direct hydrogen bonding between P and L. Clearly, for binding between two large proteins or between proteins and nucleic acids, we can expect many pairs of FG, each of which contributes about 3 kcal/mol to the total binding free energy.

Having established that the solvent-induced effect can provide a considerable contribution to the binding free energy, we may claim that in any real example this effect might operate either separately or in combination with the "lock and key" effect to produce a selective recognition of a binding site.

Figure 5 shows two identical sites on P, which from the point of view of the direct interaction (as well as δG^{H} and $\delta G_{\text{I}}^{\text{I/H}}$) will have the same probability of binding a given ligand. However, if there is at least one pair of FG in the J region with the correct orientation, one of these sites, say A, may become more favourable for binding the ligand. Using the estimate we had for $\delta G_J^{\text{HB/H}}$, the ratio of the probabilities of binding to these two sites is:

$$\frac{y_A}{y_B} = \exp[-\beta \delta G(A) + \beta \delta G(B)] \approx \exp \left[\frac{3.37}{0.592} \right] = 297. \quad (47)$$

Thus, the site A is almost 300 times more likely to bind the ligand as site B. In this case we might say that L recognizes the site A, although this recognition is not obvious from the "key and lock" model.

Figure 6 shows a slightly different situation. Here, from the point of view of the direct interaction, site C will be considered more favourable (more contacts between P and L). However, one pair of FG in the J region may provide sufficient solvent-induced driving force that will make site D more likely to bind the ligand.

Another example of solvent-induced effect is shown in figure 7. Suppose that the

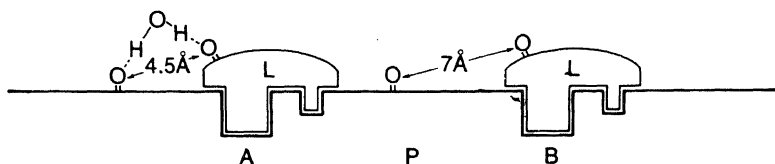


Figure 5. Two identical sites A and B on P. From the point of view of direct interaction, L will have the same binding energy with A and B. The indirect solvent-induced effect will favor binding of L to A.

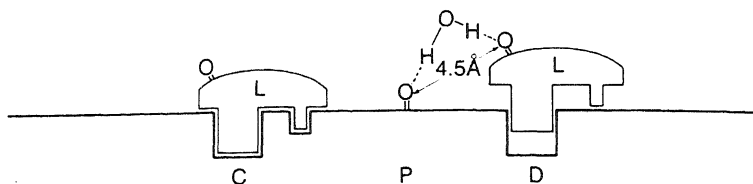


Figure 6. Two different binding sites C and D. From the point of view of direct interaction, L will favor binding to C (better fit). However, the solvent-induced effect might give preference to binding to D.

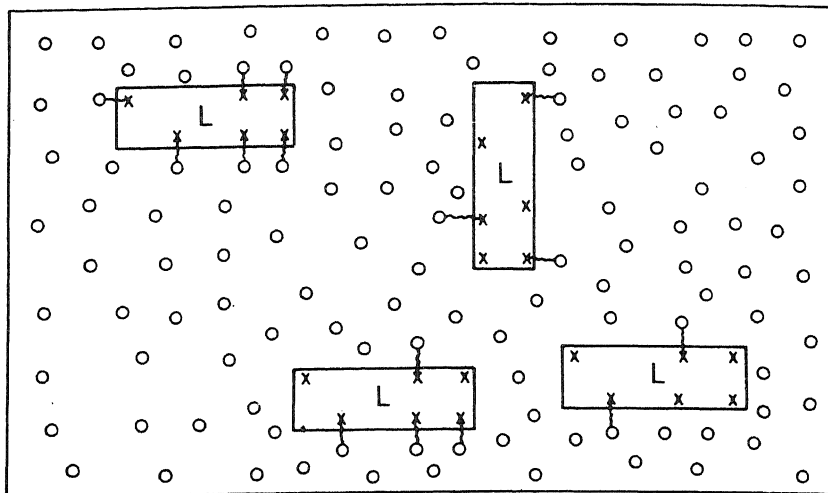


Figure 7. FG on the surface of P are distributed randomly on the surface of P so that there is no specific pattern, that can be recognized by L through direct interactions. However, indirect solvent-induced effects can give considerable preferences to certain sites (see §6 for estimates of relative probabilities to bind on different sites). Here and in figures 8, 9, and 10, an open circle represents a HB acceptor and $\times$ represents a HB donor. A line connecting $\times$ and $\circ$ represents a bridge through one water molecule.

surface of the polymer P contains FG which are more or less uniformly distributed on its surface. There are no "locks" nor any specific patterns of FG that could be recognized by the direct interaction between L and P. Thus, from the point of view of the direct interaction, all possible sites on P are nearly equally probable for binding. However, if some of these FG can form bridges through water molecules, then some specific locations on the surface of P may become preferable. The probabilities of binding to the various sites indicated in figure 7, relative to binding to an arbitrary point on the surface of P, are:

$$P(2)/P(0) = \exp \left[2 \times \frac{3.37}{0.592} \right] = 8.8 \times 10^4,$$

$$P(3)/P(0) = \exp \left[3 \times \frac{3.37}{0.592} \right] = 2.6 \times 10^7,$$

$$P(4)/P(0) = \exp \left[4 \times \frac{3.37}{0.592} \right] = 7.7 \times 10^9,$$

$$P(5)/P(0) = \exp \left[5 \times \frac{3.37}{0.592} \right] = 2.3 \times 10^{12}. \quad (48)$$

It is quite clear that even a few pairs of favorably oriented FG may lead to a very large solvent-induced preference to binding.

7. Solvent effect on self assembly

As noted in §5, there are a few distinctly different effects of the solvent on the binding thermodynamics. In §6 we chose one of these effects, which we believe can be very significant in the determination of the specificity of the binding. We now apply the same effect to describe other processes of binding and aggregation.

For simplicity, we assume that our building blocks are featureless, except for having FG in the J region that can form HB with the solvent. Two kinds of FG are assumed to occur, HB donors (denoted by $\times$ in figures 7, 8, 9, and 10) and HB acceptors (denoted by $\circ$ in the figures). These FG can form a bridge through one water molecule by means of two HB, presented in the figures by lines connecting $\times$ to $\circ$. We also assume that pairs of FG, $\times$ and $\circ$, are far apart and, therefore, operate independently.

Two examples of solvent-induced self-assembly are shown in figure 8. In (a), we have a homopolymer built up of a single subunit A, which has a given pattern of donor and acceptor FG that matches so that the solvent effect would enhance stacking of these monomers one on top of the other. In (b), we have a homopolymer of subunits A, but each monomer is rotated relative to its neighbour by an angle α . This mode of packing may or may not be periodic depending on whether there is an integer n such that $\alpha \times n = 2\pi$.

In figure 9 we demonstrate a few examples of heteropolymers. These may or may not have periodicity in the sequence of monomers (e.g., A recognizes B, B recognizes C, C recognizes A, and so on).

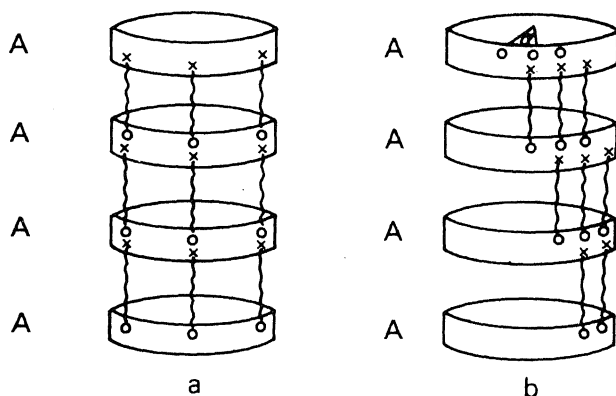


Figure 8. Self assembly of identical units to form homopolymers. (a) Stacking of identical monomers A in a regular manner to form a homopolymer. (b) Stacking of identical monomers. Each monomer is rotated by an angle α relative to its adjacent monomer.

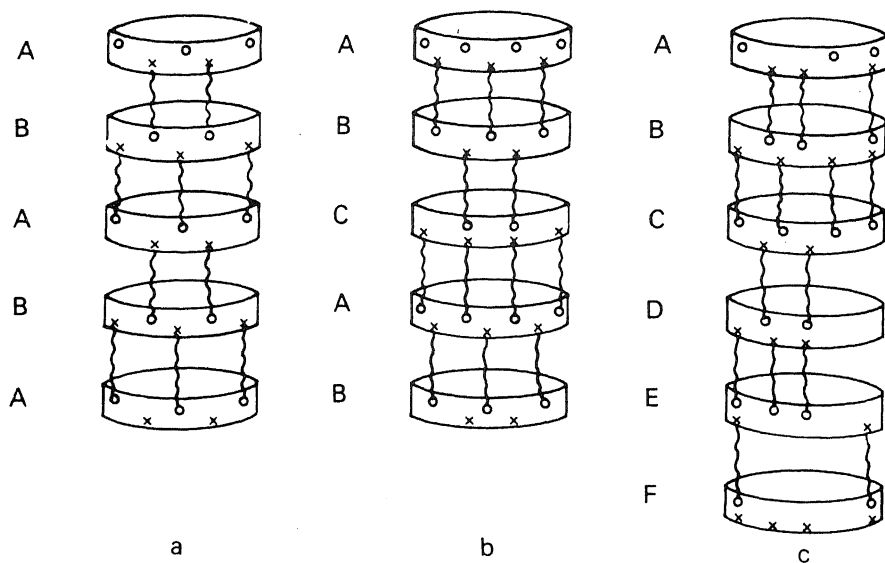


Figure 9. Various possible heteropolymers. (a) Here, monomer A recognizes B, B recognizes A, and so on. (b) Here, monomer A recognizes B, B recognizes C, C recognizes A, and so on. (c) Here, A recognizes B, B recognizes C, etc. No periodicity in the pattern of monomers.

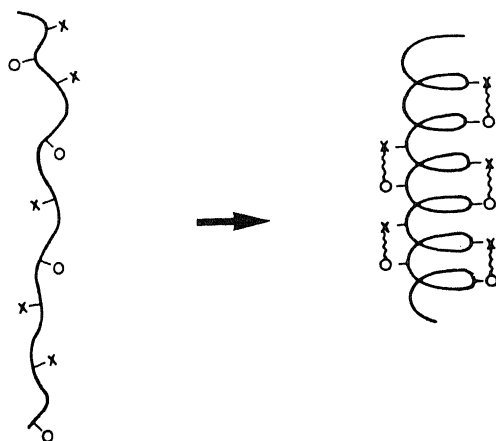


Figure 10. Possible contribution to the stabilization of a certain conformation of a biopolymer by means of hydrogen-bonded bridges through water molecules.

Clearly, association can occur to form structures other than simple stacking as shown in figures 8 and 9. The important point that should be stressed here is that, even in cases when there is no apparent *direct* means of recognition, a pattern of FG on biopolymers can provide means for indirect recognition. We can say that such a pattern of FG store information which leads to a highly specific mode of packing. Furthermore, the "expression" of this information is achieved only in aqueous solutions. We note also that, in contrast to the direct recognition which depends *only* on the properties of the monomers, the indirect recognition can be controlled also by changes in the composition of the solvent. This gives us a finer

mechanism to regulate the extent of binding or self-assembly, a mechanism which certainly confers considerable advantages over the direct recognition and which is likely to be exploited by biological systems.

Although we have endeavored to show that recognition can be achieved by purely solvent-induced effects, it is likely that in real cases both direct and indirect effects will be operating simultaneously.

8. Solvent effect on protein folding and stabilization

Much has been studied about the mechanism of protein folding by means of the direct intramolecular interactions. Also, the solvent effect has been introduced to explain the tendency of nonpolar groups to be either completely or partially removed from being exposed to the solvent by approaching each other. This effect falls within the conventional concept of HI. Here, we present also the possibility of solvent effect on the stabilization of a particular conformation due to bridges by means of water molecules. Figure 10 depicts one such example where acceptor and donor FG (denoted by $\circ$ and $\times$, respectively) are brought to a distance of about 4.5 Å where they can form two HB to a water molecule. This effect (operating in combination with others) can contribute significantly to the stabilization of a particular conformation, an effect which will be highly specific to liquid water and, as in the binding process, could be controlled by changes in the composition of the solvent.

9. Conclusion

The traditional concept of HI has been generalized to include any kind of solvent-induced effect on binding thermodynamics. We have seen that there are at least three distinctly different ways that the solvent can contribute to the binding free energy. Focusing on one of these, we have demonstrated that the solvent effect could be large and highly specific in molecular recognition processes.

Although direct recognition probably plays an important role in biochemical processes, it is inconceivable that nature would not have utilized the advantages of the solvent-induced effect. The latter, being highly specific to the composition of the solvent offers a fine way of controlling and regulating these processes. It can also be used to "switch preferences." For example, in the case of figure 6, changes in the solvent composition can change the ability of water molecules to form HB with the solute. Adding a solute which increases the ability of hydrogen bonding will give preference to site D; an opposite effect can be achieved by adding a solute that decreases the ability of hydrogen bonding, leading to preference of site C. Such a mechanism clearly has an evolutionary advantage over the conventional "lock and key" mechanism based on direct interactions.

Of course, much more effort should be expended to clarify the various contributions to the solvent-induced effect and to obtain more reliable estimates of their magnitudes. We hope that this paper will encourage further theoretical study of this topic.

Appendix A

Estimates of the volumes of the configurational space of a water molecule forming one and two HB with a given FG

In §6 we introduced the quantities η and η' to approximate some integrals over all the configurations of a water molecule that forms one or two HB with a given pair of FG. In a previous paper (Ben-Naim *et al* 1987) these quantities were estimated based on the experimental values of the second virial coefficient for water, which at room temperature is approximately:

$$B_2(T \approx 298 \text{ K}) = \frac{1}{16\pi^2} \int \{\exp[-\beta U_{ww}(\mathbf{X}_1, \mathbf{X}_2)] - 1\} d\mathbf{X}_1 \\ \approx -110 \text{ cm}^3 \text{ mol}^{-1}, \quad (\text{A1})$$

where U_{ww} is the water-water pair potential, and the integration is over all possible configurations of one water molecule (the second being at a fixed configuration denoted by $\mathbf{X}_2$). Thus:

$$\int d\mathbf{X}_1 = \int dx_1 \int dy_1 \int dz_1 \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^{2\pi} d\psi. \quad (\text{A2})$$

We now split the total range of integration in (A1) into two parts. The first is when $R_{12} \leq \sigma_{ww}$ where $\sigma_{ww} \sim 2.8 \text{ \AA}$ is the hard-core diameter of a water molecule. The second is over all configurations for which $R_{12} > \sigma_{ww}$. In this part we assume that the main contribution to the integral comes from those configurations for which the two molecules are hydrogen-bonded (and possibly additional van der Waals interaction).

Thus, we write (A1) as:

$$B_2 = -\frac{1}{16\pi^2} \int_{R_{12} \leq \sigma_{ww}} d\mathbf{X}_1 + \int_{R_{12} > \sigma_{ww}} \{\exp[-\beta U_{ww}(\mathbf{X}_1, \mathbf{X}_2)] - 1\} d\mathbf{X}_1 \\ = \frac{1}{2} \frac{4\pi\sigma_{ww}^3}{3} - \frac{8}{2} [\exp(11) - 1] \eta = -110 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{A3})$$

The first term on the RHS of (A3) is essentially half the excluded volume between two water molecules. This is estimated to be:

$$\frac{1}{2} [4\pi(2.8)^3/3] = 45.99 \text{ \AA}^3 = 27.69 \text{ cm}^3 \text{ mol}^{-1}. \quad (\text{A4})$$

The factor 8 in the second term on the RHS of (A3) accounts for the fact that there are eight identical regions from which one molecule can form a HB with a second molecule. The maximum value of the integrand is taken to be $\exp(11) - 1$ to account for both the HB energy ($\beta U^{\text{HB}} \approx 10$) and van der Waals interaction ($\beta U^{\text{vdW}} \approx 1$). Hence, we have from (A3) and (A4):

$$\eta = \frac{110 + 27.69}{4 \exp(11)} = 5.74 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \quad (\text{A5})$$

The second quantity we want to estimate is the configurational volume of a water molecule forming two HB with the two FG as in figure 3. If the two FG are oriented ideally to form two HB, then the range of configurations for the coordinates x_1, y_1 ,

and z_1 allowable for the water molecule to form one HB or two HB will be the same. Regarding the rotational configurations, we choose the following three axes of rotation – the O-O axis between the water and one FG, the O-O axis between the water and the second FG, and the axis through the oxygen of the water and perpendicular to the plane containing the three oxygens. Clearly, rotation about one of the O-O axes by 2π will not affect the HB energy for the HB along that particular axis. However, when we have a second FG and we require that the water will form a second HB with this FG, then this rotational range should be reduced from 2π to some $\Delta\alpha$. Hence, the relation between η' and η is approximately:

$$\eta' = \eta \frac{\Delta\alpha}{2\pi} \approx \eta \frac{20}{360},$$

where the choice of $\Delta\alpha \sim 20^\circ$ was taken as an average between two ranges (the so-called strong and weak HB) suggested by Dahl and Andersen (1983).

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The hydrophobic interaction between macroscopic surfaces

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Abstract. The aim of this paper is to review our current level of knowledge of the interaction between hydrophobic surfaces immersed in water. The strong attractive forces observed between such surfaces have generally been referred to as "the hydrophobic interaction". Although the precise origin of this force has not yet been determined, we will examine recent experimental studies and relate them to other phenomena like cavity formation and repulsive hydration forces.

Keywords. Hydrophobic interaction; hydrophobic force; cavitation; surfactant monolayers; force measurements; hydration force.

1. Introduction

The hydrophobic nature of solute molecules often determines their solution properties; for example, it provides the driving force for molecular self-assembly of amphiphilic molecules into micelles, vesicles and bilayers (Tanford 1973; Franks 1973, Israelachvili *et al* 1976). The hydrophobic interaction also plays a crucial role in determining the detailed conformation of proteins in solution (Kauzmann 1959). Co-operative surfactant adsorption onto surfaces is also largely due to hydrophobic interaction between the hydrocarbon regions of the molecules (Cases and Mutaftschiev 1968; Herder *et al* 1987).

Although the hydrophobic force between solute molecules is used to explain solution behaviour this force has, until recently, seldom been considered important when discussing surface interactions. The reason for this is that solute-solvent interactions, in contrast to electrical double-layer and van der Waals forces, are believed to be of very short-range, decaying over a few diameters of solvent molecules at most. That the hydrophobic effect between macroscopic surfaces is of significant range and strength, however, was clearly illustrated some years ago by Laskowski and Kitchener (1969). These authors pointed out that although surface methylation of silica does not alter the van der Waals interaction or the electrical charge at the silica-water interface, the macroscopic wetting properties of the surface are drastically changed. The Derjaguin-Landau-Verwey-Overbeck (DLVO) theory applied to water films on silica predicts wetting for both surfaces (Pashley and

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Kitchener 1979), which is clearly not the case. Laskowski and Kitchener conclude, therefore, that some other structural or solvation effect must occur at the methylated surface and that this effect must extend some distance from the interface in order to overcome van der Waals and double-layer forces.

Blake and Kitchener (1972) attempted to estimate the range of the hydrophobic interaction on methylated silica by observing the rupture of an aqueous film produced on compressing an air bubble against the surface. They found an upper limit to the range of about 64 nm. Above this thickness the films were stabilized by repulsive double-layer forces.

More recently, a series of experiments has been carried out in an attempt to quantitatively measure the strength and range of the hydrophobic interaction between solid surfaces. The development of a remarkable surface forces apparatus (Israelachvili and Adams 1978) has made it possible to directly measure such forces. This apparatus measures the force as a function of separation between two mica surfaces in a crossed-cylinder configuration with a distance resolution of 0.1–0.2 nm and a sensitivity of 0.1 μN . The measured force F_c is related to the free energy of interaction between parallel, flat surfaces (G_f) (Derjaguin 1934),

$$F_c/R = 2\pi G_f, \quad (1)$$

where R is the local geometric mean radius of curvature of the interacting surfaces.

In these experiments the muscovite mica surfaces were made hydrophobic either by adsorption of surfactants from solution or by deposition of Langmuir-Blodgett films. The forces measured between hydrophobic surfaces have in all cases been much more attractive than can be explained by a combination of van der Waals and double-layer forces (the DLVO-theory).

The strength of this attraction is the cause of the stronger cohesion between hydrophobic surfaces in water than in air (Shchukin *et al* 1981), despite the fact that the van der Waals attraction should be larger in air (Hough and White 1980). Furthermore, this strong hydrophobic interaction appears to be long-range and will thus play a crucial role in many systems including the interaction of biologically important molecules in solution.

The hydrophobic force is of direct relevance to froth flotation where air bubbles, which are inherently hydrophobic ($\gamma_{sv} = 72 \text{ mJm}^{-2}$) interact with hydrophobed mineral particles across an aqueous surfactant solution during particle approach and attachment. The subtle control of this attachment process is the key to efficient mineral separation with this widely used technique. It should be pointed out that the van der Waals force between a mineral particle and an air bubble interacting across water is always repulsive and the occurrence of bubble attachment therefore indicates the presence of an additional, attractive force.

There are many other technically important areas in which hydrophobic interaction is involved in critical processes, for instance oil recovery, detergency, food emulsification, paint production and in the deposition of well-defined multimolecular Langmuir-Blodgett films for use in electronic devices (eg LEDs).

In the following section we will review some of the recent experiments carried out on the direct measurement of the hydrophobic interaction between macroscopic surfaces.

2. Direct measurements of the macroscopic hydrophobic interaction

The first direct evidence for the presence of a strong, long-range interaction between hydrophobic surfaces was obtained when forces between mica surfaces coated with an adsorbed monolayer of cetyltrimethylammonium ions (CTA⁺) were measured (Pashley and Israelachvili 1981; Israelachvili and Pashley 1982, 1984). These surfaces were found to be highly charged and only moderately hydrophobic, with a water contact angle of about 60°. There was an exponential double-layer repulsion between the surfaces as illustrated in figure 1. At small separations attractive van der Waals forces should produce a force maximum at a separation of about 2 nm and an adhesive primary minimum at $D = 0$. However, the force maximum observed was at much larger distances and, in addition, the final primary minimum adhesion was much stronger than for the mica/water case.

In the theoretical curve in figure 1 the van der Waals force was assumed to be given by a simple non-retarded Hamaker equation: $F/R = A/D^2$, where the Hamaker constant A was taken to be 2×10^{-20} J. This value is, if anything, an overestimate and is still insufficient to cause the attraction observed.

The hydrophobic force law was determined in this system from the analysis of a series of experiments carried out under different CTAB solution conditions. In order to do so the theoretical DLVO curve (obtained by a fit to the measured forces at larger separations) was subtracted from the total force to obtain an estimate of the range and magnitude of the interaction. The force law obtained in

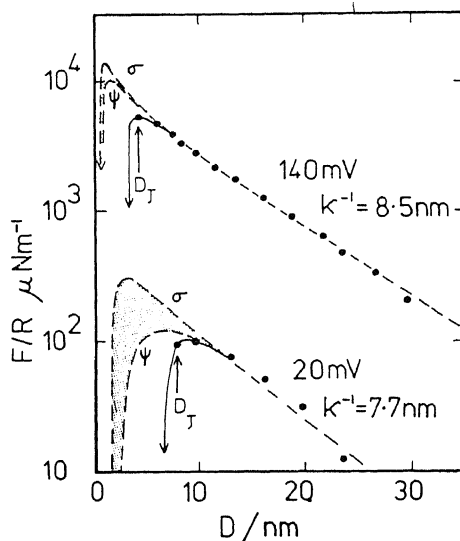


Figure 1. Measured repulsive force (normalized by radius) between two CTA⁺-coated surfaces in aqueous solutions of KBr. The upper force curve was measured at pH ~ 5.6 and a CTAB concentration of 2.5×10^{-5} M (plus KBr at 1.3×10^{-3} M). The lower force curve was measured at pH ~ 9.0 and a CTAB concentration of 10^{-4} M (in addition to 1.5×10^{-3} M KBr). The dashed lines are the theoretical DLVO force laws expected where a *nonretarded* Hamaker constant of $A = 2 \times 10^{-20}$ J has been assumed. Note that the force barriers occur much farther out than expected, indicating the existence of a strongly attractive force at these distances where the van der Waals force should be almost negligible.

this way could be fitted by an exponential function with a decay length of about 1 nm (see figure 2). These experiments clearly demonstrate that the hydrophobic interaction is much stronger than the expected van der Waals interaction and extends to at least 10 nm.

More recent experiments on the mica-CTAB system using carefully purified surfactant (Christenson and Claesson, unpublished results), have produced surfaces of almost zero charge and with a water contact angle close to 90°. The attractive force observed is qualitatively similar but extends to even larger distances. This recent result in fact is in closer agreement with results using double-chain surfactant monolayers to be discussed below.

Strongly hydrophobic surfaces were obtained by depositing a monomolecular layer of dioctadecyldimethylammonium (DDOA⁺) ions onto the mica surface using the Langmuir-Blodgett procedure. The deposited layer is stable in aqueous solutions up to several days due to the strong electrostatic bonds between the negatively charged mica surface (one negative lattice charge per $\sim 0.5 \text{ nm}^2$) and the cationic headgroups as well as due to the strong cohesive forces between the hydrophobic tails. The area per molecule in the deposited layer was found to be about 0.5 nm^2 as determined by ESCA and transfer ratio measurements (Claesson *et al* 1986a). The advancing water contact angle on such a 2 nm thick surfactant layer is about 94°. Direct force measurements showed that the surfaces were only

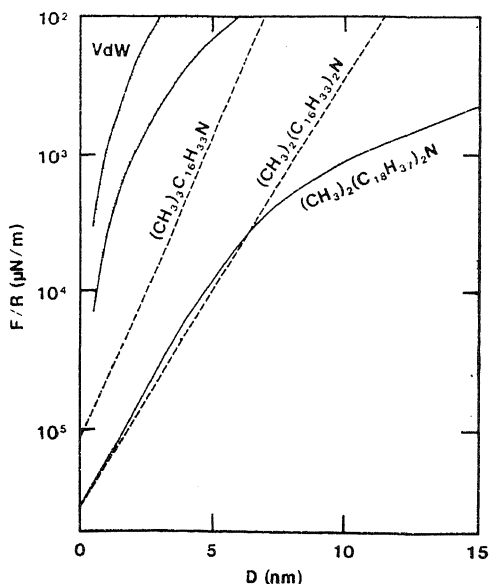


Figure 2. A comparison between the magnitude of the hydrophobic interaction measured in three different systems and the nonretarded van der Waals force, plotted on a logarithmic scale. The limits of the van der Waals force have been calculated using Hamaker constants of $2.2 \times 10^{-20} \text{ J}$ (as for mica/water/mica) and $5 \times 10^{-21} \text{ J}$ (as for hydrocarbon/water/hydrocarbon). The lines are for surfaces coated with cetyltrimethyl ammonium ions $((\text{CH}_3)_3(\text{C}_{16}\text{H}_{33})_2\text{N}^+ \gamma_{\text{SL}} = 11 \text{ mN/m})$, dihexadecyldimethylammonium ions $((\text{CH}_3)_2(\text{C}_{16}\text{H}_{33})_2\text{N}^+ \gamma_{\text{SL}} = 34 \text{ mN/m})$ and dioctadecyldimethylammonium ions $((\text{CH}_3)_2(\text{C}_{18}\text{H}_{37})_2\text{N}^+ \gamma_{\text{SL}} = 34 \text{ mN/m})$. The first two surfaces were obtained by adsorption of the surfactant from solution, the third by Langmuir-Blodgett deposition.

weakly charged, but the dominant feature of the interaction was found to be a strong attractive force measurable out to separations of about 30 nm (Claesson *et al* 1986a). The experimental technique used in this particular case determines the slope of the force rather than the force itself. This slope is then, of course, proportional to the pressure between flat surfaces (taking the derivatives of equation (1)). Figure 3 shows a plot of the slope of the attraction (after subtraction of the weak double-layer repulsion) as a function of distance (see also figure 2).

Addition of potassium bromide to a concentration of 10^{-2} M reduced the range of the double-layer force, which made the total force purely attractive with the hydrophobic interaction dominant at all surface separations. The net hydrophobic interaction was only marginally reduced by the increased electrolyte concentration (see figure 3). This contrasts with the strong salt-dependence of attractive double-layer forces between one DDOA⁺-coated mica surface and one bare mica surface (Claesson *et al* 1987) and shows that the measured attraction is not due to the surfaces having opposite charge.

Surfaces having an even larger water contact angle of about 110° are obtained when a monolayer of a polyfluorinated double-chain cationic surfactant [N-(α -trimethylammonioacetyl)-0,0'-bis(1H,1H,2H,2H-perfluorodecyl)-L-glutamate chloride] is deposited onto mica. In figure 3 the slope of the hydrophobic force for this system shows that the attraction is even more long-range than for the hydrocarbon surfaces (Christenson *et al*, to be published). Clearly, the hydrophobic force is orders of magnitude stronger than the expected van der Waals force and seems to increase in strength with surface hydrophobicity as determined by the water contact angle.

A strong hydrophobic interaction has also been observed between mica surfaces coated with monolayers of a range of other surfactants including dodecyl-dimethyl-

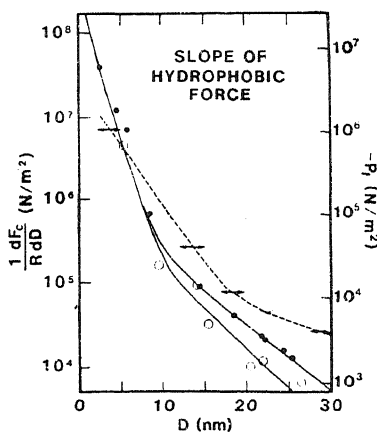


Figure 3. The slope of the hydrophobic interaction measured between dioctadecyl-dimethylammonium ion-coated mica surfaces (solid lines) and between fluorocarbon coated surfaces (dashed line). Filled circles are points obtained in conductivity water and open circles after addition of potassium bromide to 10^{-2} M. Any double-layer repulsion has been subtracted out. The slope of the force between curved surfaces is proportional to the pressure between flat surfaces, as shown on the right-hand ordinate. As can be seen, the effect of increasing the salt concentration 300 times is almost negligible. Note the logarithmic scale.

amine oxide and primary amines (Herder *et al.* to be published), and dimethyldihexadecyl ammonium acetate (see figure 2) (Pashley *et al.* 1985). Hence, it is extremely unlikely that the strong attraction observed in all cases is due to some contamination present in all surfactant samples or in all the types of purified water used in these experiments.

Further support for the view that this attraction is a true hydrophobic interaction comes from the observation that it is completely removed on adsorption of a second surfactant layer with polar or ionic head groups facing the solution. This is illustrated in figure 4 for the case of pentaoxyethylenedodecyl ether (Claesson *et al.* 1986b) and is a general property of all the surfactants studied. Other compounds which have been shown to have a similar effect include primary amines and alkylamine oxide (Herder *et al.* to be published), quaternary amines (Pashley and Israelachvili 1981) and insulin (Claesson *et al.* to be published).

3. The hydrophobic force law

In this section we attempt to describe the distance dependence of the hydrophobic interaction between surfaces in a simple mathematical form. These expressions are useful for *estimating* the hydrophobic interaction expected between comparable hydrocarbon-coated surfaces and are a first step towards bridging the large gap between theory and experiment.

It appears that the hydrophobic interaction at distances less than about 7–8 nm can be reasonably well fitted with an exponential function. The free energy of interaction between flat surfaces can therefore be described roughly by the

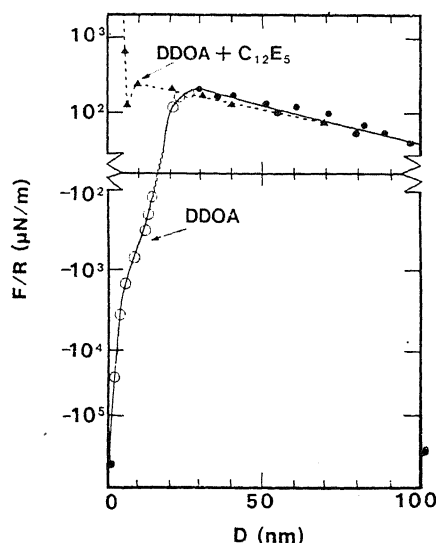


Figure 4. The total force measured between dioctadecyldimethylammonium ion-coated surfaces in water before (○) and after (▲) addition of $6 \cdot 10^{-5}$ M pentaoxyethylenedodecyl ether ($C_{12}E_5$). The $C_{12}E_5$ adsorbs to the hydrophobic surfaces and completely removes the hydrophobic interaction, while the double-layer repulsion is unchanged.

relation:

$$G_f = -C \exp(-D/\lambda). \quad (2)$$

The decay constant, λ , is slightly above 1 nm. The other constant, C increases with surface hydrophobicity and is roughly equal to twice the solid-liquid interfacial energy (γ_{SL}) estimated from contact angle measurements. However, at lower distances, the observed hydrophobic interaction decays more slowly than that indicated by (2). One way of including the weaker tail in a simple manner is to use an exponential function with two decay constants. For instance the hydrophobic interaction between two DDOA-coated mica surfaces in 10^{-2} M KBr (see figure 3) is well described by the relation:

$$G_f = -5.8 \times 10^{-2} \exp(-D/1.2) - 1.0 \times 10^{-3} \exp(-D/4.5) \text{ (J/m}^2\text{)}, \quad (3)$$

where D is in nm. A power law function with a distance dependence of D^{-2} to D^{-3} can also be used to fit the measured hydrophobic interaction over a range of distances at least reasonably well.

4. Hydrophobic interaction and cavity formation

The possible formation of a cavity around two highly solvophobic surfaces in contact (the contact angle of the solvent on the surface should be larger than 90°) has been considered theoretically (Yaminsky *et al* 1983) and also observed experimentally between glass surfaces in mercury (Yushchenko *et al* 1983). It was shown that the creation of a vapour cavity between these surfaces is thermodynamically favoured when the surfaces are closer together than a certain critical distance, D_c , which depends among other things on surface hydrophobicity. However, the energy barrier for cavity formation is very large and no cavity should form until the surfaces are less than a few tenths of a nanometer apart. Once the cavity has formed the energy barrier for its disappearance is large. Consequently, the surfaces must be separated to distances considerably larger than D_c before the cavity disappears.

The main predictions of Yaminsky *et al* have in fact been nicely confirmed by recent measurements. Between fluorocarbon surfactant-coated mica surfaces many small and irregular shaped cavities do form once the surfaces are brought into contact, or about 1–2 nm from contact. These cavities remain between the surfaces upon separation until they suddenly disappear at separations of a few micrometers. However, it is important to note that during measurement of the hydrophobic attraction, prior to the surfaces coming into contact, no cavities between the surfaces have been observed.

Between less hydrophobic DDOA⁺-coated surfaces no detectable cavity forms between the surfaces when they are brought into contact. However, when separating the surfaces from molecular contact a cavity does form. This cavity is considerably smaller than those formed between fluorocarbon-coated surfaces, and upon separation, disappears at smaller surface separations.

Between CTA⁺-coated mica surfaces no cavity has yet been observed, but further investigations are under way to establish whether or not a cavity does form in this case. We would not expect cavity formation for surfaces with water contact angles significantly less than 90° .

We conclude that the measured hydrophobic interaction is not due to the presence or formation of small vapour cavities between the surfaces. However, the hydrophobic attraction and cavity formation are related to each other. Furthermore, the hydrophobic force measured between strongly hydrophobic surfaces is not a thermodynamic equilibrium force since in the true equilibrium state a cavity should be present between the surfaces. For all practical purposes, however, the force behaves as an equilibrium force in the sense that it is reproducible between experiments and between repeat measurements. The reason for this is, of course, that the energy barrier the system has to overcome in order to reach the thermodynamically stable state is too large and the system remains in its metastable state.

5. Speculations around the molecular mechanism underlying the hydrophobic interaction between macroscopic surfaces

The pressure, P , inside a liquid may be considered to be composed of one kinetic component, P_k , trying to separate liquid molecules and one cohesive component, P_c , acting so as to keep the liquid molecules held tightly together. For a simple liquid one has (Hill 1962):

$$P = P_k + P_c = nkT + \frac{n^2}{6} \int_0^{\infty} r \frac{du_2(r)}{dr} g_2(r, n, T) 4\pi r^2 dr, \quad (4)$$

where n is the number density of liquid molecules, g_2 the pair distribution function and u_2 the pair interaction potential. In water P_k is of the order of 1300 atmospheres or 1.3×10^8 N/m². Since P equals the external pressure of 1 atmosphere it follows that the cohesive pressure also is about 1300 atmospheres. Obviously one has two large contributions to the total pressure which together with the external pressure exactly balance each other. Let us assume that two hydrophobic surfaces in close proximity perturb the local balance of pressures. Clearly, this could potentially give rise to large forces comparable in strength to the measured hydrophobic attraction (figure 3). Take the hydrophobic interaction between DDOA⁺-coated mica surfaces as an example. At a surface separation of ~ 1 nm the attractive pressure is about 20 atmospheres and at 20 nm about 0.05 atmospheres. Clearly only a very small perturbation of the delicate balance between the kinetic and the cohesive pressures is sufficient to account for the observed hydrophobic interaction. Taking into account that cavities might form between hydrophobic surfaces in contact and that the hydrophobic interaction, at least for highly hydrophobic surfaces, is measured in a metastable state, it is easy to visualize perturbations of the balancing pressure terms occurring at larger distances. If this concept is correct, a hydrophobic interaction between surfaces occurs as a result of the system going in the direction of forming a cavity and this tendency will depend on the proximity of the two interacting surfaces.

A complementary "microscopic" view of the hydrophobic interaction may also be developed. Thus, we may assume that a hydrophobic surface will induce an increased, dynamic ordering of water molecules near the surface. The extensive hydrogen-bonding network of water will propagate this enhanced ordering out

from the surface until it has decayed to its bulk value. The approach of the two hydrophobic surfaces further enhances this dynamic ordering between the surfaces and displaces water molecules from the interlayer region to bulk solution. The overall effect of this is to decrease the free energy of the system thus giving rise to an attractive force. It is instructive to calculate the free energy gain per water molecule, g_t , transferred from the interlayer region to bulk, needed to account for the observed attraction. It is given by:

$$g_t = (\partial G_f / \partial D) / (\partial N / \partial D), \quad (7)$$

where N is the total number of water molecules between flat surfaces per unit area. This free energy gain for DDOA⁺-coated surfaces is shown as a function of surface separation in figure 5. Clearly, the large hydrophobic interaction observed corresponds to a free energy gain of only fractions of kT per water molecule. Thus, it cannot be expected that water between hydrophobic surfaces is different from bulk water in any way which could easily be detected using for instance Monte Carlo or molecular dynamics simulations. Once again, it appears that very minor differences between bulk water and water between two surfaces can give rise to enormous forces.

According to this view the attractive hydrophobic force is essentially of the same type as the repulsive hydration force observed between hydrophilic surfaces. One would thus expect a gradual change from a repulsive hydration force to an attractive hydration force (hydrophobic force) with increasing surface hydrophobicity (Israelachvili 1985). Some support for this hypothesis comes from an investigation of the temperature-dependent interaction between surfaces coated

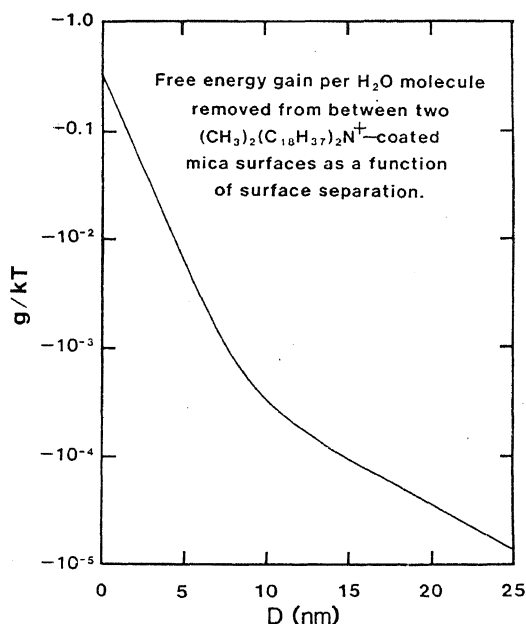


Figure 5. The free energy of transfer per molecule of water from between two hydrophobic surfaces to bulk. The values were calculated from the results of figure 3. As can be seen, the energy per water molecule is very small indeed.

with pentaoxyethylenedodecyl ether (Claesson *et al* 1986b). At low temperatures the hydration force between ethylene oxide units was found to be purely repulsive. However, as the temperature was increased part of the force curve turned attractive. This could be explained by assuming an essentially hydrophobic type of hydration around the ethyleneoxide chains. For the case of ethylene oxide the two large changes in ΔH_f and $T\Delta S_f$ and occurring on pushing the surfaces together nearly cancel each other in $\Delta G_f = \Delta H_f - T\Delta S_f$. Thus a small change in temperature changes the sign of ΔG_f and the repulsion turns into an attraction.

It is perhaps pertinent at this point to consider the oscillatory forces observed between mica surfaces in aqueous electrolyte solutions (Pashley and Israelachvili 1984). These forces have a periodicity close to the diameter of a water molecule and may be regarded as superimposed on the repulsive hydration force. However, these forces are not observed when the surface is rough on the molecular scale and are not seen between lipid bilayer-coated mica surfaces (Horn 1984; Marra and Israelachvili 1985). It is, therefore, likely that any such oscillations would be smeared out for the hydrophobic monolayer surfaces as well. In any case, the strong overall attraction present in these systems would make the detection of oscillatory forces very difficult.

6. Future studies

There remains much to be done experimentally (as well as theoretically, of course). As an example, the temperature dependence of the hydrophobic interaction must be thoroughly investigated. Such a study would provide information about the changes in enthalpy and entropy involved when two hydrophobic surfaces come together in water. This in turn would give some clue as to the molecular origin of the hydrophobic force.

Another important study would involve the interaction between weakly hydrophobic surfaces. Such a study might clarify if a hydrophobic interaction arises suddenly at a given surface hydrophobicity or if there is a gradual change from a large repulsive hydration force, as observed between mica surfaces in concentrated electrolyte solutions, to (i) weakly repulsive and attractive hydration forces, as observed between ethylene oxide layers, and (ii) strongly attractive hydrophobic forces as observed between surfaces coated with surfactant monolayers.

A third area, not discussed here, involves the possibility of solvophobic forces in non-aqueous media. Do such forces exist in any other solvent or only in strongly hydrogen-bonding liquids or are they unique to water?

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Photoreactions in hydrophobic pockets

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Abstract. Organic chemists have long recognized the important role that reaction media play in controlling rates, product distributions and stereochemistry. Recently, much effort has been directed towards the use of organized media to modify reactivity as compared to that in isotropic liquids. Judicious selection of a given organized system for a given application requires sufficient understanding of the properties of the organized media themselves and those of the substrate interactions therein. The multimolecular aggregation of hydrophobic solutes in water could prove to be of immense value to the organic chemist. The aggregation of simple olefinic systems in water would enable photocyclo-addition to compete efficiently with the various other modes of decay of the short-lived excited state. Investigations of a few systems (dimerization of coumarins, stilbenes and alkylcinnamates) in our laboratory have been successful and they bring to light the significance of the hydrophobic effect. One of the most accepted manifestations of the hydrophobic interactions is probably the formation of micellar aggregates in aqueous solutions. Micelles provide a unique interface between aqueous and non-aqueous phases at which the non-polar solute can orient itself. While intermolecular orientation at micellar interfaces can provide selectivity in dimerization reactions, intramolecular orientation can be utilized to bring about selectivity in unimolecular photo-transformations. Such examples are presented.

Keywords. Photoreactions; association in aqueous media; micellar effect; selectivity in reactions; hydrophobic effect.

1. Introduction

Hydrophobic interactions are often claimed to play a central role in most biological processes. It is described as the indirect contributor to the intermolecular forces arising due to the surrounding aqueous or mixed aqueous solvent (Ben Naim 1980). The so-called 'direct' forces are those which operate in the gas as well as in solution phases, namely van der Waals' interactions, London forces and Columbic forces. Interestingly, the non-polar solutes present in the aqueous phase experience, in addition to the 'direct' forces, yet another intermolecular force termed as the hydrophobic force, solely due to the surrounding aqueous medium, tending to cluster them together. Traditionally, the hydrophobic effect has been ascribed to the relatively unfavourable entropy of dissolution of non-polar solutes in water in comparison with non-polar solvents, as a result of the formation of ordered 'ice berg' regions of water surrounding such solutes (Frank and Evans 1945). An interesting consequence of this is reflected in the tendency of apolar solutes to

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aggregate in the aqueous phase, thus minimizing the loss of entropy. Although the hydrophobic effect has been viewed as an entropy effect in the past, recent reports portray enthalpy as the overriding contributor (Abraham 1982; Wertz 1980). The multimolecular aggregation of hydrophobic solutes in water could prove to be of immense value to the organic chemist. Probably, the appreciation of hydrophobic interactions began with the discovery of micelle formation, and their introduction as a reaction medium, an area which has stimulated considerable interest among chemists (Ramnath *et al* 1985; Ramamurthy 1986). More recently, however, the uniqueness of the aqueous phase as a reaction medium was demonstrated (Rideout and Breslow 1980). Although the utility of the aqueous phase as a reaction medium for thermal reactions could be appreciated, at the time we began our studies its use for photoreactions was yet to be demonstrated. With this aim in mind, we undertook an estimation of the potential of aqueous and micellar phases as media for photoreactions. In the present article the results of our investigations are described with the aim of illustrating and highlighting the significant role of hydrophobic interactions in altering the course of photoreactions in aqueous and micellar phases.

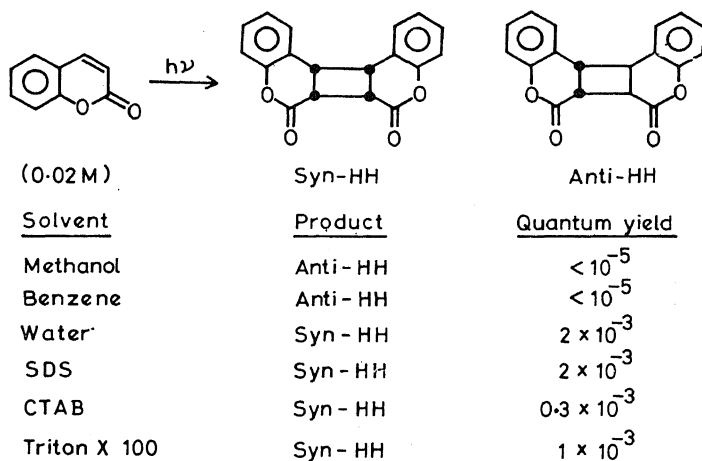
2. Water: A unique and useful solvent

The preassociation of simple organic solutes in aqueous media as a result of hydrophobic interactions can be utilised in bringing about efficient bimolecular reactions. The presence of microheterogeneous regions of high local concentrations of solutes as well as the formation of a transition state with a smaller surface area would serve as driving forces for such bimolecular reactions. A dramatic illustration of this phenomenon was made in the Diels-Alder reactions of cyclopentadiene with a variety of dienophiles in aqueous solutions (Rideout and Breslow 1980). Efficient cycloaddition occurred even when the reactants were poorly soluble and formed a separate phase in water (Breslow *et al* 1983). Moreover, a remarkable selectivity between the endo and exo cycloadducts was demonstrated (Breslow *et al* 1983; Grieco *et al* 1983). This was attributed to a superposition of the specific orientational effect along with the polarity effect of water. Prompted by the above results, efforts towards the utilisation of the preassociation of organic solutes in water in bringing about efficient and selective photodimerizations were thought to be in order. The aggregation of simple olefinic systems in water would enable photocycloaddition to compete efficiently with the various other modes of decay of the short-lived excited state. Thus, hydrophobic aggregation should lead to exciting prospects for the excited state chemists:

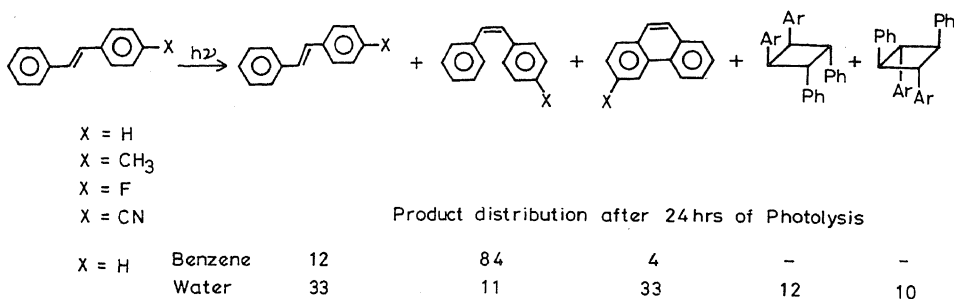
The effectiveness of pre-association in bringing about efficient photodimerization was originally demonstrated for concentrated aqueous solutions of dimethylthymine and tetramethyl uracil by Morrison and coworkers (Kleopfer and Morrison 1972; Otten *et al* 1977). Efficient photodimerization which resulted from the singlet excited state of these solutes was incompatible with a mechanism involving a diffusion controlled reaction between the short-lived singlets and the ground state molecules and hence required the presence of preformed aggregates in aqueous solution. The presence of such aggregates was detected by osmometric measurements and efficient photodimerization was attributed to the ground state stacking

of these solutes in concentrated aqueous solution. In fact such a hydrophobic aggregation could also be expected in very dilute aqueous solutions of poorly soluble organic solutes and this could prove to be much more dramatic by bringing about photodimerization in very dilute solutions. Investigations of a few such systems in our laboratory have been successful and they bring to light the significance of the hydrophobic effect (S Devanathan and V Ramamurthy, unpublished results; Muthuramu and Ramamurthy 1982; Syamala and Ramamurthy 1986). Coumarin forms one such system with moderate solubility in water. The photodimerization of coumarin in non-aqueous media is known to be less efficient, yet regiospecific depending on the polarity of the solvent. While *anti*-head-head dimer was the major isomer in non-polar solvents, the *syn*-head-head was the major component in polar solvents ($\Phi_{\text{dim}} \approx 10^{-5}$ at 0.02 M; scheme 1). Dramatically, a single product, namely, the *syn*-head-head dimer crystallised out when dilute aqueous solutions of coumarin were photolysed ($\Phi_{\text{dim}} \approx 10^{-3}$ at 0.01 M). Such an enhanced reactivity was unexpected based on polarity considerations alone. In line with the reported photodimerization of coumarin in non-aqueous solvents, the reaction was presumed to be singlet derived. In order for dimerization to compete efficiently with the other deactivating modes of the short-lived excited singlet state either the life-time of the singlet state should be longer in aqueous solution or reaction must occur from preformed aggregates. The failure to observe a deviation from Beer's law, which would support the aggregation proposal, does not completely rule out the possibility of ground state aggregation, as it is known from earlier investigations that ground state aggregation need not always be accompanied by a deviation in Beer's law. On the other hand, coumarin in aqueous solution was found to emit strongly in contrast to its poor emission in non-aqueous solvents, thus suggesting that the excited state lives long enough for emission to compete with other modes of decay. Based on the above arguments it can be concluded that the enhanced efficiency of coumarin dimerization is a combined effect of its increased lifetime and the presence of hydrophobic aggregation in water.

Investigations of poorly water-soluble systems could lead to much more exciting results, and this was, in fact exemplified by the photodimerization of stilbene and alkyl cinnamates in dilute aqueous solution. Of the various reactions that originate



Scheme 1



Scheme 2.

from their excited singlets, geometric isomerization and cyclization are the main competitors in dilute non-aqueous solutions of stilbene. Photodimerization is totally absent in organic solvents and begins to be important only above a concentration of 0.1 M. Surprisingly, a very dilute aqueous solution ($\sim 10^{-6}$ M) of *trans*-stilbene underwent dimerization upon 24 hours of photolysis (scheme 2). In a similar manner, the formation of two isomeric dimers could be detected in a dilute aqueous solution ($\approx 10^{-5}$ M) of *cis*-stilbene within 2 hours of photolysis. The two isomeric dimers detected by gas chromatographic analysis and H^1 -NMR proved to be the same as those formed in benzene irradiations, with the same ratio. The lack of stereoselectivity in aqueous media probably shows that the geometry of the excimer remains the same in aqueous and non-aqueous solvents. A follow-up of the product yield with respect to time revealed that isomerization preceded dimerization for *cis*-stilbene and the resulting *trans* isomer dimerized efficiently. The possible dimerization from floating micro-crystals of *trans*-stilbene was ruled out based on control irradiations of *trans*-stilbene crystals which proved to be photostable. As in the previous cases efficient dimerization of stilbene from their excited singlet state warrants ground state aggregation. In contrast to coumarin, where an increased lifetime (singlet) was proposed based on its high emission yield, the strongly fluorescent *trans*-stilbene underwent a noticeable drop in its emission yield in aqueous solution. This probably indicates the presence of additional decay channels, namely excimer formation and dimerization of the preformed aggregates, which deactivate the excited singlet state of stilbene.

Alkyl cinnamates behaved in a manner similar to the stilbene in that near quantitative dimerization occurred in dilute aqueous solution ($\sim 10^{-3}$ M, scheme 3), while non-aqueous solutions of identical concentration led only to isomerization. The head-head dimer, δ -truxinate was the major isomer detected by H^1 -NMR. The dimerization efficiency in aqueous solution was high in contrast to that of the neat liquid although the ratio of the isomeric dimers were identical in both the cases. The efficient dimerization in the aqueous phase reveals it to be a manifestation of the hydrophobic aggregation of solutes. To support the aggregation proposal in the case of stilbenes and cinnamates, experiments were devised with the use of additives expected to alter the aggregation behaviour in predictable ways. It is known that lithium chloride increases hydrophobic aggregation while guanidinium chloride serves to de-aggregate organic and biomolecules in water (von Hippel and Schleich 1969). Noticeable consequences of such perturbations were found in the resulting dimer yields (tables 1 and 2). In both the cases investigated, namely *cis*-stilbene and *trans*-ethyl cinnamate, lithium

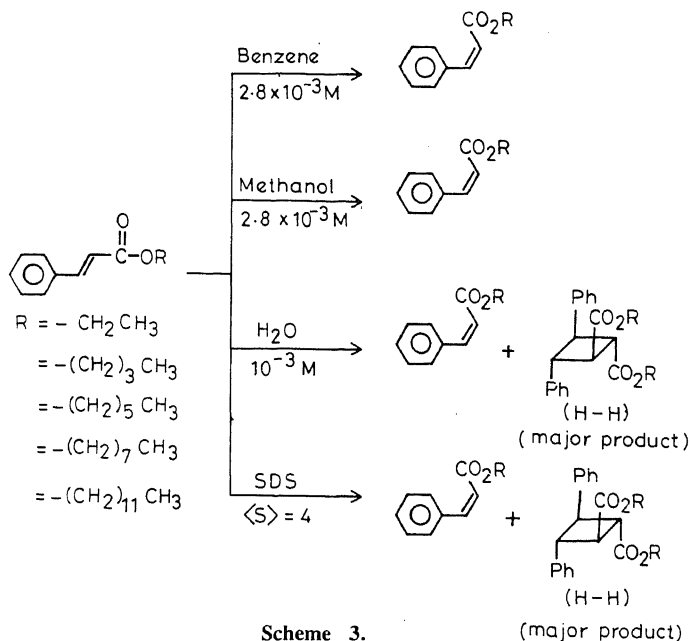


Table 1. Product distribution upon photolysis of stilbene in water in presence of additives^{a,b}.

Condition ^c	Geometric isomers (%)		Phenanthrene (%)	Dimer (%)	
	<i>cis</i>	<i>trans</i>		A	B
<i>cis</i> -stilbene in benzene	91	5	4	—	—
<i>cis</i> -stilbene	11	33	33	12	12
<i>cis</i> -stilbene + LiCl (3)	7	27	25	25	17
<i>cis</i> -stilbene + guanidinium chloride (3M)	11	21	53	8	6
<i>cis</i> -stilbene + β -cyclodextrin (1:10)	29	71	—	—	—
<i>cis</i> -stilbene + SDS $\langle S \rangle : 1^d$	36	26	33	3	2

^aAnalysed by g.c.; Error limit: $\pm 2\%$.

^bIrradiated for 24 hr using a 450 W medium pressure mercury lamp in a merry-go-round.

^cAll solutions had identical concentration (5.5×10^{-4} M) and matched OD, and were irradiated simultaneously.

^d $\langle S \rangle$ = Occupancy number.

chloride enhanced the dimer yield while guanidinium chloride reduced it noticeably. In a similar manner, the encapsulation of these molecules into the hydrophobic cavity of β -cyclodextrin would isolate them from the other molecules thus preventing dimerization totally. This was indeed observed upon addition of an excess of β -cyclodextrin to aqueous solutions. Thus the presence of hydrophobic aggregation in dilute aqueous solution of stilbene and *trans*-cinnamates was proved to be the principal factor responsible for their efficient dimerization. The results

Table 2. Photolysis of ethyl cinnamate in aqueous media in the presence of additives.

Media ^{a,b}	Percentage of products ^c		
	<i>cis</i>	<i>trans</i>	Dimer
Water	7	22	70
Water/lithium chloride (3M)	5	21	74
Water/guanidinium chloride (3M)	10	30	60
Water/ β -cyclo-dextrin (1:2)	56	43	—
Water/ β -cyclo-dextrin (1:5)	58	41	—

^aSolutions were of optical density.^bIrradiations were done using Rayonet reactor fitted with RPR = 254 nm lamps. All samples irradiated for 24 hr.^cBased on GC analysis.

described above demonstrate the potential of commonly available water as a solvent for photoreactions and stress the need for an increased appreciation of its utility. Needless to say, hydrophobic interactions are the major contributions which make water a unique and useful solvent for photo and thermal reactions.

3. Micelles as reaction vessels

One of the most widely accepted manifestations of hydrophobic interactions is probably the formation of micellar aggregates in aqueous solution. Surfactant molecules with polar head groups and hydrophobic tails tend to cluster up in an aqueous medium forming an oil-like pool of hydrocarbon chains from which the polar head groups stick out and get solvated by water. Such spherical aggregates are called micelles and these form at and above a certain concentration range known as critical micellar concentration (CMC). The most interesting property of a micelle lies in its ability to solubilise non-polar solutes by providing a hydrophobic pocket for their residence in aqueous and non-aqueous phases at which the non-polar solute can orient itself suitably. The following section is devoted to an illustration of the potential of micelles as reaction vessels with the use of a few photoreactions investigated in our laboratory where striking alterations were brought about by the micellar media.

3.1 Intermolecular orientation at micellar interface

Apart from solubilizing apolar solutes, the micellar interface serves to orient them with their polar moieties exposed to the aqueous exterior, while the non-polar groups get buried in the interior. Such an orientation in fact organizes the micelle-solubilized reactants in a predictable manner and is expected to lead to remarkable regioselectivities in micellar reactions. A dramatic illustration of this phenomenon which also proves to be of great synthetic utility is the regiospecific

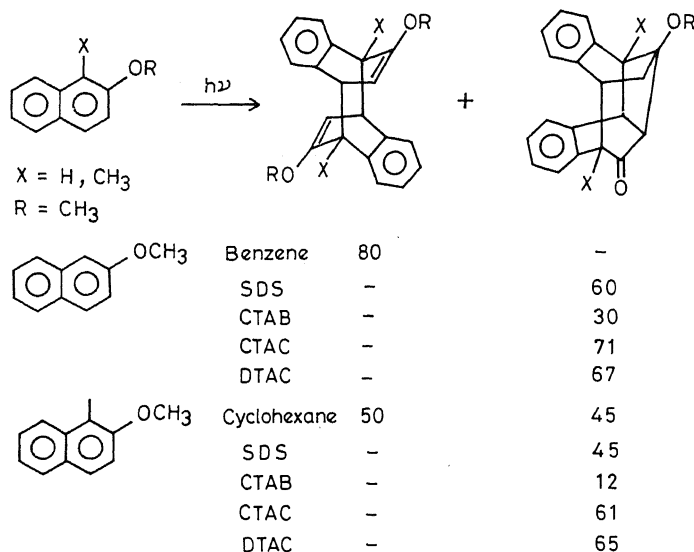
photodimerization of cyclopentenones in potassium dodecanoate (KDC) micelles, where exclusive formation of the head-head dimer was observed (Lee and de Mayo 1979; Berenjian *et al* 1982). This is in contrast to the dimerization behaviour in cyclohexane where the head-tail dimers predominate. Although an improved yield of the head-tail dimer could be brought about by increasing the polarity of the solvent used for irradiations, the total reversal of regioselectivity observed in KDC micelles is far more than expected based on polarity considerations alone and can only be attributed to the pre-orientation of the solute molecules at the micellar surface.

While investigating the potential of micelles as reaction vessels in bringing about regioselective photodimerization reactions, two factors need to be borne in mind. Along with the pre-orienting effect at the micellar interface, polarity of the micelle would also play a role in deciding the regiochemical outcome of a reaction, especially for cases which are known to be sensitive to polarity effects. The situation is well-exemplified by the photodimerization of coumarin in micellar media (Muthuramu and Ramamurthy 1982, 1984). The reaction efficiency which was poor in organic solvents improved to a great extent in the various micelles investigated, presumably due to high local concentration of coumarin in the micelles. Interestingly, a single dimer (*syn*-head-head) crystallized out of the micellar solutions during irradiation. This was unexpected because the hydrocarbon-like interior of the micelle was likely to give the *anti* head-head dimer, the product of irradiation in non-polar solvents. The most obvious alternative, that of a reaction occurring in the aqueous phase with the micelle serving only as the storage site, was ruled out based on the insensitivity of the dimer yield to changes in polarity of the aqueous phase upon addition of sodium chloride and its sensitivity to an increase in the occupancy number of coumarin. Thus the regioselective dimerization could be accounted for by invoking a certain degree of water penetration into the micellar interior, and hence providing a polar environment for the coumarin molecule. It is to be noted that the required polarity for the reaction can be provided if the coumarin molecules align themselves at the micellar-water interface.

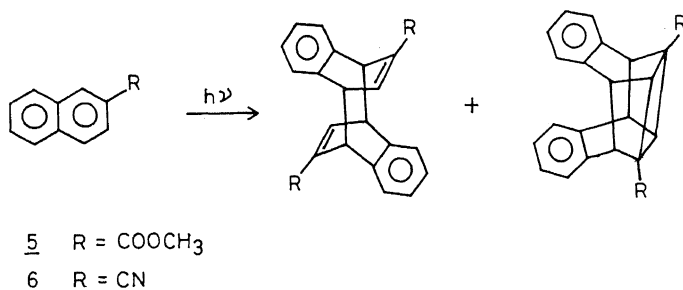
Although the regiochemical outcome of the above mentioned investigation was explainable based on a combination of the pre-orientational and polarity effects of the micelles, a desire to estimate the relative efficiencies of each in bringing about regioselectivity in micellar reactions is irresistible. In this regard, we proceeded to estimate the effectiveness of pre-orientational effect in bringing about regioselectivities (Muthuramu *et al* 1983; Ramesh and Ramamurthy 1984a; Ramnath and Ramamurthy 1984). Quite predictably a few systems were chosen where the regiochemistry of photodimerization was independent of the polarity of the medium. During the course of our efforts we were led not only to appreciate the potential of the pre-orientational effect in bringing about regioselectivity, but also its limitations in the presence of other overriding factors.

The photodimerization of 2-substituted naphthalenes which, in principle, could lead to the *cis* and *trans* dimers was chosen for investigation as it was known to give polarity independent dimer yields (scheme 4). In non-aqueous solvents the *trans* dimer is the major product with the formation of trace amounts of products derived from the *cis*-dimer. Irradiation of 2-substituted naphthalenes 1-4 in SDS, CTAB, CTAC and DTAC micelles gave rise to the ketones derived from the *cis*-dimers as

the sole product. In fact a precipitation of the *cis*-dimer itself was observed in the case of 2-ethoxynaphthalene in CTAC micelles. In a similar manner, the substrates 5 and 6 gave rise to cage products derived from the *cis* dimer when irradiated in the same micelles (scheme 5). The enhanced dimerization efficiency was explainable by the local concentration effect. A pronounced increase in the dimerization efficiency in CTAC when compared to that in CTAB could be anticipated due to the well-known effect of Br^- in bringing about an increased intersystem crossing, thus shortening the singlet lifetime, leading to a decreased reactivity (Ramesh and Ramamurthy 1984b). When the counterion is changed to Cl^- , the heavy atom induced intersystem crossing is negligible and hence dimerization efficiency is



Scheme 4.



<u>5</u>	benzene / i-propanol	25 %
	SDS	57 %
	CTAC	36 %
<u>6</u>	benzene / hexane	15 %
	CTAC	38 %

Scheme 5.

restored. The remarkable regioselectivity could only be explained based on the orientation of the 2-substituted naphthalenes at the micellar interface in a manner shown in figure 1, which is to be expected based on the amphiphilic nature of the solute. The present example thus serves as an illustration of the potential of pre-orientational effect in bringing about regioselectivity.

In order to examine the effectiveness of micelles in orienting molecules and to explore the possible limitations, we undertook the investigation of yet another system viz. 7-alkoxy and 4-methyl 7-alkoxy coumarins. These systems were appropriately chosen to suit our goal because these photodimerize in organic solvents to give rise to a single dimer (*syn* head-tail) from their excited singlet states, irrespective of the polarity of the medium. It was anticipated that the introduction of a long alkyl chain at the alkoxy portion would help in anchoring the alkoxy chain in the interior of the micelle, while the carbonyl group would be turned towards the surface of the micelle. Such an orientation would facilitate the formation of the head-head dimer (figure 2). Our expectations of obtaining a head-head dimer from the irradiations of 7-alkoxy and 4-methyl 7-alkoxy coumarins in SDS, CTAB and CTAC micelles were in vain, the photolysis in all cases leading to the *syn*-head-tail dimer as the sole product, with a greater efficiency expected on the basis of the local concentration effect (table 3). The results thus demonstrate the insufficiency of the hydrophobicity introduced in terms of the alkyl chains to overcome the molecular forces to induce a reversal in the regioselectivity. We further attempted to bring about the expected reversal in selectivity by improving the degree of hydrophobicity, by introducing still longer chains. With these systems (7) also the formation of head-head dimer could not be achieved (scheme 6). Surprisingly, the substrate 7 with the longest alkyl chain,

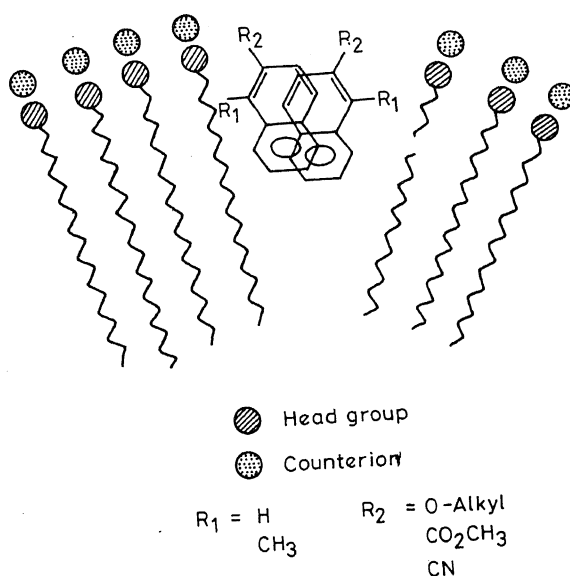


Figure 1. Orientation of 2-substituted naphthalenes at the micellar interface.

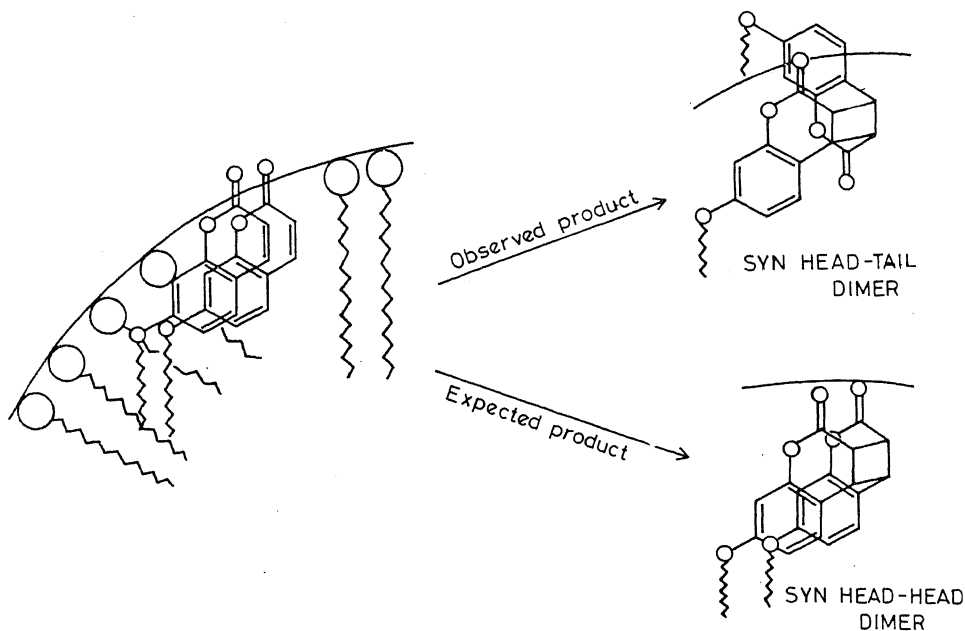


Figure 2. Expected orientation of long chain 7-alkoxycoumarins at the micellar interface.

which had a problem in getting solubilized into SDS micelles at high concentrations, upon photolysis gave rise to a mixture dominated by the *anti*-head-tail dimer. In fact, substrates with alkyl chains longer than the surfactant chains themselves are expected to be adsorbed on the surface of the micelle with the alkyl chain curled up inside the micelle. As a result of such an adsorption, two neighbouring molecules present on the surface could probably encounter each other only in a manner suitable for the formation of the *anti*-head-tail dimer (figure 3). In conclusion, the failure to obtain the expected head-head dimer in these systems by the induction of pre-orientation exposes the limitations of the micellar alignment effect when the molecular forces operating to dictate the regiochemical outcome are overwhelmingly stronger than the hydrophobic interactions tending to orient the molecule at the micellar interface.

3.2 Intramolecular orientation at micellar interface: Conformational and cage effects

The hydrophobicity of the micellar interior which serves as the driving force for solubilization of apolar solutes, helps to prevent their escape from the interior of the micelle, by providing a more favourable environment for their existence, than the aqueous exterior. As a consequence of this, the short lived radicals formed in a reaction are forced to stay in the same volume of the micelle long enough to encounter their counterparts. In other words, micelles act 'super cages' by trapping the radicals inside and facilitating their recombination. The 'cage effect' of micelles was utilized in a very imaginative manner in the photolysis of dibenzyl ketones (DBK) by Turro and co-workers (Turro *et al* 1980). Out of the three products AA,

Table 3. Photodimerization of 7-alkoxycoumarins in organic, aqueous and micellar media.

Compound	Media	(Coumarin) (M)	Duration of irradiation ^a (hr)	Product formed ^b	Yield ^c (%)
7-O-Methyl- coumarin (1)	Methylene chloride	0.25	72		40
	water	2.1×10^{-3}	24	Syn HT	65
	SDS (0.032 M)	1.1×10^{-3}	5		70
	CTAB (0.01 M)	6.0×10^{-3}	72		10
	methylene chloride/ benzophenone (0.1 M)	0.15	72	No reaction	
7-O-butyl- coumarin (2)	Chloroform- <i>d</i>	0.5	24	Syn HT	35
	water	10^{-5}		No reaction	
	SDS (0.05 M)	1.4×10^{-2}	30	Syn HT	50
	CTAB (0.02 M)	1.1×10^{-2}	30		5
	chloroform- <i>d</i> /benzo- phenone (0.2 M)	0.25	30	No reaction	
7-O-hexyl- coumarin (3)	Chloroform- <i>d</i>	0.75	45	Syn HT	75
	water	10^{-5}		No reaction	
	SDS (0.05 M)	1.4×10^{-2}	45	Syn HT	42
	CTAB (0.025 M)	1.6×10^{-2}	45	Syn HT	5
	chloroform- <i>d</i> /benzo- phenone (0.2 M)	0.25	45	No reaction	
7-O-heptyl- coumarin (4)	Chloroform- <i>d</i>	0.25	50	Syn HT	54
	water	Not soluble	50		
	SDS (0.05 M)	6×10^{-3}	50	Syn HT	50
	CTAB (0.025 M)	6×10^{-3}	50	Syn HT	6
	chloroform- <i>d</i> /benzo- phenone (0.2 M)	0.25	50	No reaction	
7-O-octyl- coumarin (5)	Chloroform- <i>d</i>	0.25	50	Syn HT	25
	water	Not soluble			
	SDS (0.05 M)	6×10^{-3}	50	Syn HT	25
	CTAB (0.025 M)	6×10^{-3}	50	Syn HT	5
	chloroform- <i>d</i> /benzo- phenone (0.2 M)	0.25	50	No reaction	
7-O-dodecyl- coumarin (6)	Chloroform- <i>d</i>	0.25	50	Syn HT	17
	water	Not soluble			
	SDS (0.05 M)	5×10^{-3}	50	Syn HT	10
	CTAB (0.025 M)	5×10^{-3}	50	Syn HT	5
	chloroform- <i>d</i> /benzo- phenone (0.2 M)	0.25	50	No reaction	

^aAll irradiations were conducted in Pyrex vessels by using a 450 W medium pressure mercury lamp.^bStructures of the dimers were identified by their spectral properties.^cYields presented correspond to TLC isolated yields.

AB and BB that are possible from the combination of the benzyl radicals A and B, which result from the photolysis of the unsymmetrical DBK (A-CO-B), the exclusive formation of AB was found in HDTCl micelles, demonstrating the efficiency of the super cage provided by the micelle. The cage effect, as expected, was proportional to the hydrophobic volume and hence to the surfactant chain

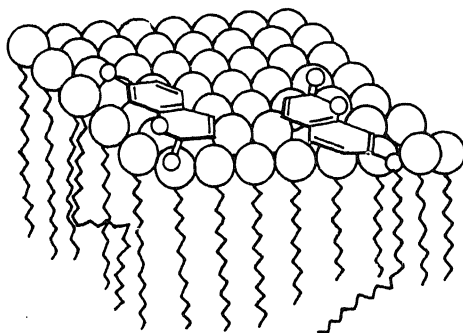
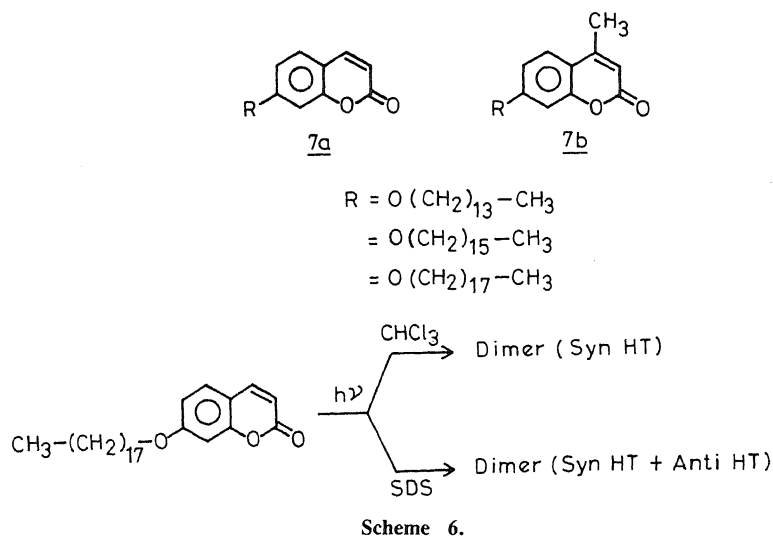
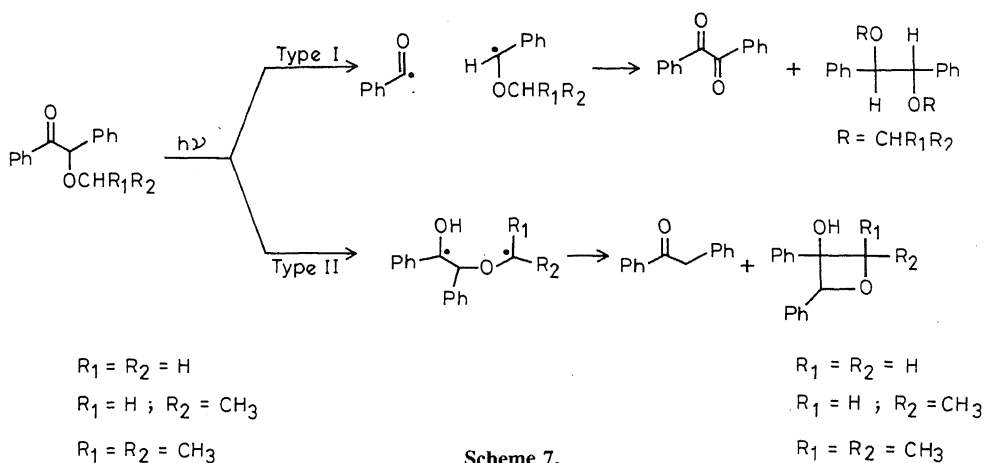


Figure 3. Pre-orientation of long chain 7-alkoxycoumarins at the micellar phase when the chain is longer than the surfactant alkylchain.

length. The cage control of a radical reaction could lead to very exciting prospects as was demonstrated by the achievement of an isotopic enrichment during the photolysis of DBK (Turro *et al* 1980). Another interesting consequence of the cage effect which hitherto has not received much attention was demonstrated in our laboratory in the photolysis benzoin alkyl ethers in a variety of micelles (S Devanathan and V Ramamurthy, unpublished results).

Benzoin alkyl ethers are known to undergo Norrish type I reaction as the only photoreaction in organic solvents (scheme 7). The type II reaction, if feasible in these substrates, is not observed probably due to the overwhelmingly faster type I process. The incorporation of such a system into the super cage provided by the micelle, is expected to suppress the type I process, the initially formed α -cleavage radical being facilitated to recombine to regenerate the starting benzoin ether. Under such circumstances, the normally slow type II process would become detectable, provided the conformation of the molecule is suitable for the



H-abstraction process. In line with our expectations, photolysis of benzoin methyl ether in CTAB and CTAC micelles under conditions of low occupancy revealed the formation of the type II products along with the para-rearranged product of the starting benzoin ether in low yields (table 4). The super cage provided by the micelles probably allows the radicals to live long enough to tumble over before recombination, thus accounting for the small fraction of the rearranged product. The observed dependence of the type II products yields upon the occupancy number (table 5) and the hydrophobic volume (table 6) of the micelle gave support for the operation of cage control. It may be noted that the operation of cage control alone does not suffice to explain the type II products. Out of the two conformations

Table 4. Photoproduct distribution of benzoinmethylether in various micelles.

$ \begin{array}{c} \text{Ph} \\ \parallel \\ \text{C} \\ \diagup \quad \diagdown \\ \text{MeO} \quad \text{H} \end{array} \xrightarrow[h\nu]{(S)=1} $	$ \begin{array}{c} \text{MeO} \quad \text{OMe} \\ \quad \\ \text{Ph}-\text{C}-\text{C}-\text{Ph} \\ \quad \\ \text{H} \quad \text{H} \end{array} $	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{Ph}-\text{C}-\text{CH}_2-\text{Ph} \end{array} $	$ \begin{array}{c} \text{OH} \\ \\ \text{Ph}-\text{C}-\text{C}-\text{Ph} \\ \quad \\ \text{Ph} \quad \text{O} \end{array} $	(RP)
(Type I)		(Type II)		
$\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^- \text{Na}^+$ (SDS)	42	24	12	6
$\text{CH}_3(\text{CH}_2)_{10}\text{COO}^- \text{K}^+$ (KDC)	38	17	10	5
DTAB	44	27	6	6
DTAC	50	30	5	5
$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{NH}_4^+ \text{Br}^-$ (CTAB)	23	13	3	42 (5)
$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{NH}_4^+ \text{Cl}^-$ (CTAC)	23	8	4	52 (4)

Type I / Type II Product ratio (a) depends on the micellar size
(b) independent of the nature of the micelle.

Table 5. Type I vs type II photoproduct distribution of benzoinmethylether in various media.

	Type I		Type II		
Benzene	18 (24)	58	—	—	—
Methanol	26 (10)	62	1	—	—
CTAB $\langle 0.5 \rangle$	13	6	3	47	6
$\langle 1 \rangle$	23	13	3	42	5
$\langle 2 \rangle$	24	16	10	37	9
$\langle 4 \rangle$	37	24	14	18	7

Type I / Type II Products ratio depends on $\langle S \rangle$ in CTAB and CTAC and independent in SDS and DTAB.

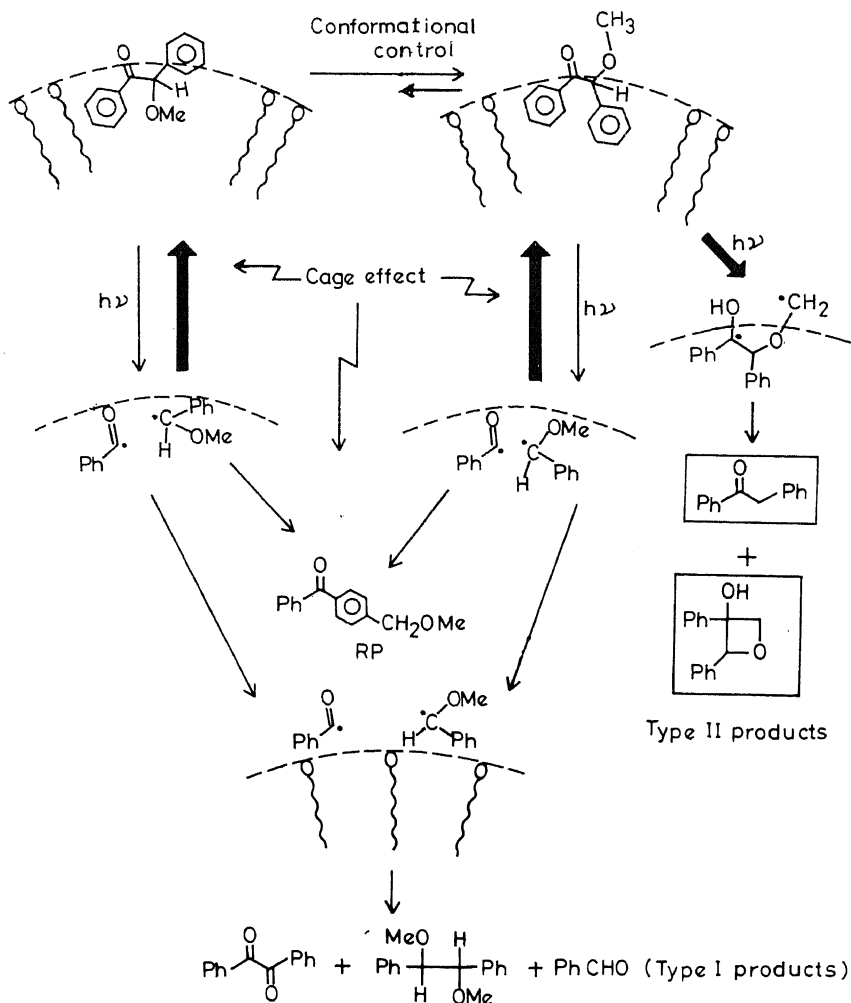
Table 6. Photoproduct distribution of benzoinoctylether in various micelles.

$\langle S \rangle = 1$				
<u>Micelle</u>				
Sodium decyl sulphate	61	35	—	<5
Sodium dodecyl sulphate	69	28	—	<5
Potassium decanoate	62	36	—	<5
Potassium dodecanoate	55	34	—	<5
DTAB	64	32	—	<5
DTAC	62	36	—	<5
CTAB	28	15	47	<5
CTAC	34	17	45	<5

A and B shown in figure 4 for the benzoin alkyl ether, the specific orientation of a particular conformer B at the micellar interface (probably due to the need for the polar oxygens of the carbonyl and alkoxy groups to point towards the aqueous phase), would lead to the formation of the type II products, as this conformation is the one favourable for the H-abstraction process. In order to investigate the validity of proposing such a conformational control in micelles, we went on to introduce longer alkyl chains on the alkoxy moiety, which would prefer to reside in the interior of the micellar core, thus attempting to populate conformer A to increasing extents. In such a case, even in the presence of a cage control, there is no possibility of observing the type II reaction. To our great delight photolysis of benzoin octyl ether in CTAB and CTAC micelles, gave rise only to the para-rearranged product (table 7) showing that the initially formed α -cleavage radicals had the only choice of recombining either with or without rearrangement,

Table 7. Photoproduct distribution of benzoinoctylether as a function of the occupancy number of the micelles.

		$\text{Ph}-\text{C}(=\text{O})-\text{CH}(\text{Ph})-\text{O}(\text{CH}_2)_7-\text{CH}_3 \xrightarrow{h\nu} \text{PhCHO} + \text{Ph}-\text{C}(\text{OR})_2-\text{Ph} + \text{Ph}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{CH}_2\text{OR}' + \left\{ \begin{array}{l} \text{PhH}_2\text{C}-\text{C}(=\text{O})-\text{Ph} \\ \text{Ph}-\text{C}(\text{OH})(\text{Ph})-\text{C}(\text{R}')-\text{Ph} \end{array} \right\}$			
CTAB	$\langle S \rangle$				
	0.5	26	12	47	<5
	1.0	28	15	42	<2
	2.0	42	20	28	<2
	4.0	46	24	22	<2
DTAB	0.5	63	35	-	<2
	4.0	65	32	-	<2


Figure 4. Conformational preference for the short chain benzoinalkylethers at the micellar interface.

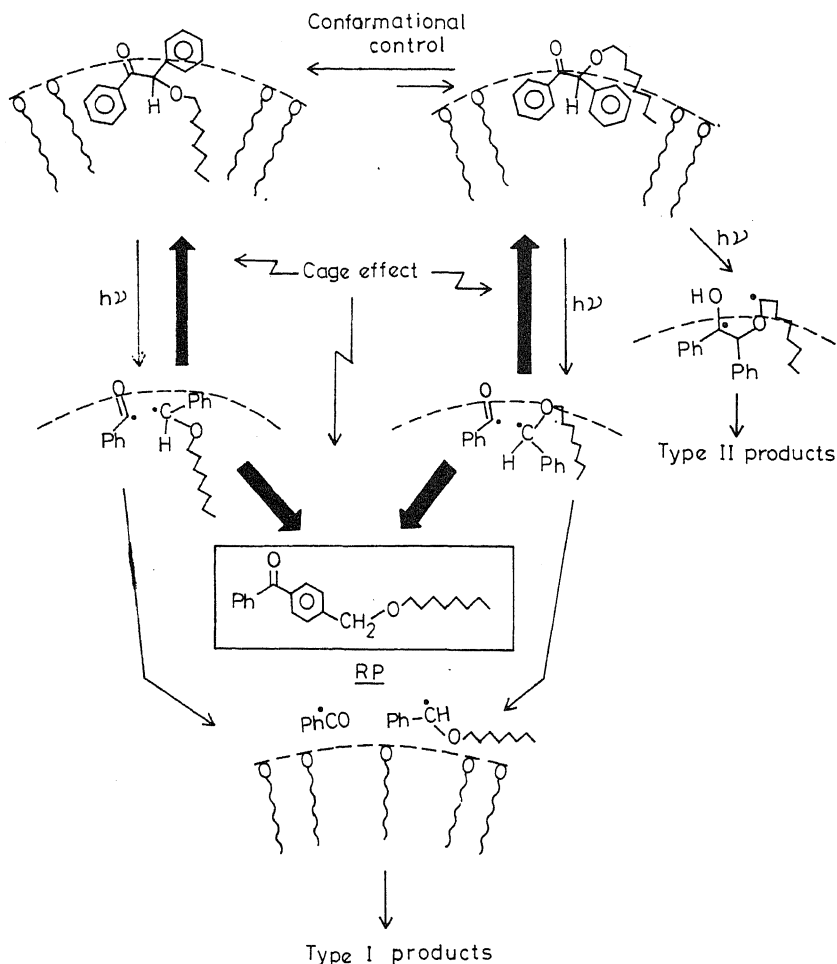


Figure 5. Conformational preference for the long chain benzoinalkylethers at the micellar interface.

thus generating benzophenones as the only products apart from the starting material itself (figure 5). The results of the present investigation reveal that excellent conformational control can be achieved in the micellar phase by a suitable tailoring of the substrates.

In conclusion it may be stated that the increased utilisation of aqueous and micellar phases for photoreactions may prove to be of much more interest and wider scope than the use of organic solvents themselves. Much remains to be understood in the field of chemistry in organized media.

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The effect of hydrophobic-lipophilic interactions on chemical reactivity. 9. Putting the spotlight on lipophilic forces in solvent-effect studies

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Abstract. The hydrolytic rate constants of the *p*-nitrophenyl esters of acetic, octanoic, dodecanoic and hexadecanoic acids in six aquiorghano binary mixtures of graded compositions at various initial substrate concentrations were measured and discussed in terms of the hydrophobic-lipophilic interactions between the substrate molecules and the organic cosolvents which were MeOH, Me₂SO, 1, 4-dioxane, 1,2-dimethoxyethane, *n*-propanol and *t*-butanol. The accelerating or retarding effects of the organic cosolvents on the rate constants of hydrolysis were found to be directly related to the lipophilicities of the solvents which were changed either by changing the content (ϕ) or the nature of the organic cosolvent. The classification or ordering of the six solvents on the basis of their solvent effects were found to conform to the lipophilicity order derived from Rekker's Σf values. The results support the proposition that lipophilic interactions can play an important role in solvent effects of aqueous binaries.

Keywords. Hydrophobic-lipophilic interactions; chemical reactivity; solvent-effect studies; hydrolysis rate constant; lipophilicity order.

1. Introduction

Solvent effects of aquiorghano binary mixtures on the hydrolytic behavior of carboxylic derivatives have interested or intrigued many physical and organic chemists, and much elegant work has been done on this subject (e.g. Elsemongy *et al* 1981, Guthrie 1973, Murakami *et al* 1977, Oakenfull 1973, Oakenfull and Fenwick 1974, Singh *et al* 1981, Holterman and Engberts 1983, Jiang *et al* 1984, 1985, Fan *et al* 1985). These effects can be very complicated and even capricious sometimes, thus in addition to the more usual notions, the concept of hydrophobic interactions has to be invoked to rationalize or interpret the results (e.g. Engberts 1982, Oakenfull and Fenwick 1974, 1977, 1979, Jiang *et al* 1984, 1987). The present work on solvent effects is an attempt to reveal contributions from hydrophobic-lipophilic interactions (hereafter abbreviated to lipophilic interactions† clearly and

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† Hydrophobic-lipophilic interactions are time and again simply referred to as hydrophobic interactions because (1) the lipophilic component (van der Waals interactions between the hydrocarbon portions of molecules) of hydrophobic-lipophilic interactions are often not considered to be so important (see, e.g., Ben-Naim 1980, Franks 1975, Oakenfull and Fenwick 1977, Shapiro and Ohki 1974, Tanford 1980), and (2) it is exceedingly difficult to experimentally assess the relative importance of these two forces. The present authors are among those who believe that under certain circumstances the contributions from lipophilic forces should not be overlooked (see, e.g., Diederich *et al* 1986, Jiang *et al* 1987). In order to call our readers' attention to lipophilicity in the present work, we choose to use the word "lipophilic" as the shortened form of the term "hydrophobic-lipophilic" without any intention of overemphasizing the importance of lipophilicity or playing down the importance of effects derived from changes in water structure (hydrophobicity).

in a relatively simple manner, without implying that other forces are of less importance.

Suppose we divide the solvation effects of the organic component in an aquiorghano solvent into two parts: (1) its solvation effects on the reagent, i.e., in our case, its effects on the nucleophile OH^- , and on the cation Na^+ ; (2) solvation effects on the organic substrate. The latter sometimes might again be composed of two parts: (a) a general effect involving heteroselective solvation (Reichardt 1979) brought about by lipophilic forces; (b) a specific solvation with lipophilic interactions as one of the contributing forces (*vide infra*). Then, by (1) comparing the hydrolytic behavior of ester substrates with different chain lengths under otherwise identical conditions and (2) using organic components of different lipophilicities (Rekker 1977; Jiang *et al* 1984; Menger and Venkataram 1986) for aquiorghano solvents with different compositions, it might be possible to demonstrate convincingly the significance of lipophilic interactions between the organic substrate and solvent molecules without disregarding other important solvent properties such as dielectric constant or other polarity parameters, pH, and hydrogen-bonding ability etc.

However, there is another basic and important phenomenon which should be taken into account carefully before we can proceed with the aforementioned approach, namely, the aggregation of long-chain substrates in aggregating solvents. Aggregation and self-coiling have been found to profoundly affect hydrolytic behavior and other properties of organic molecules (e.g. Menger and Portnoy 1968, Blyth and Knowles 1971, Guthrie 1973, Murakami *et al* 1977, Jiang *et al* 1984, 1985, Menger and Venkataram 1986, Shobha and Balasubramanian 1986.) Therefore, for long chain substrates in aggregating media, only the rate constants of their "monomeric" forms can be compared with those of their shorter counterparts. Fortunately, it is usually possible to determine fairly precisely the "critical aggregate concentration", or CAgC (*vide infra*; see also figure 1), from $\log k$ vs. initial [substrate] plots, thus rate constants of the "monomeric" forms can be obtained when they are measured in the concentration range below CAgC.

On the basis of the above mentioned considerations, we reckoned that a systematic collection and a full analysis of all the rate data obtained from different solvent systems with graded compositions might reveal contributions from lipophilicity in solvent effects. We believe this goal has been achieved.

The *p*-nitrophenyl esters of acetic, octanoic, dodecanoic, and hexadecanoic acids, hereafter abbreviated as C2, C8, C12 and C16 were used as substrates in this study. Six organic components were used for the aqueous binaries, namely, MeOH, *n*-PrOH, *t*-BuOH, 1,4-dioxane, 1,2-dimethoxyethane (DME), and Me_2SO . Composition of the binary mixtures are expressed by ϕ , the volume fraction of the organic component of the aqueous-organic solvent, e.g., for a 60:40 (v/v) organic: H_2O mixture, $\phi = 0.60$.

2. Experimental

p-Nitrophenyl carboxylates with various chain lengths were prepared by methods described previously (Jiang *et al* 1984).

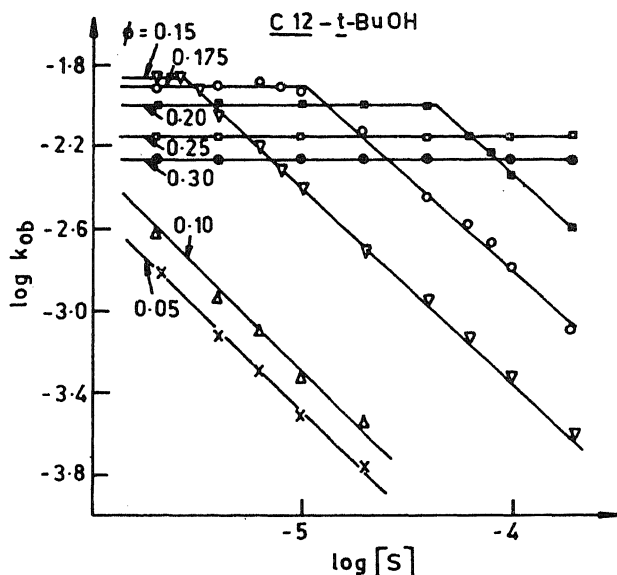


Figure 1. Hydrolysis of C12 in various proportioned *t*BuOH-H₂O mixtures at different initial [S]. Plot of $\log k_{ob}$ vs $\log [S]$ at different ϕ 's indicated by numbers.

Water was deionized and all organic solvents were purified by the usual methods as described elsewhere (Perrin 1980).

Aqueous 0.01 M NaHCO₃-NaOH solution containing 2% NaCl with pH = 11.70 was used as the buffer solution which was mixed with the organic solvent in various proportions. The pH values of the binary solvent mixtures are listed in table 1. The volume fractions of the organic solvents in the binary mixtures are expressed as ϕ values as mentioned in the introductory remarks.

2.1 Kinetics

Kinetic measurements at 35°C were performed on a Perkin-Elmer 559 spectrophotometer equipped with a thermostatted cell holder. The wavelength used for

Table 1. pH values of the binary solvent mixtures at 25°C; for $\phi = 0.00$, pH = 11.70

	$\phi = 0.05$	0.01	0.15	0.175	0.20	0.25	0.30	0.40	ΔpH^a
MeOH	11.70	11.71	11.72		11.73	11.73	11.74		0.04
<i>n</i> -PrOH	11.77	11.85	11.92	11.96	11.98	12.03	12.07		0.37
<i>t</i> -BuOH	11.74	11.83	11.92	12.12	12.02	12.08	12.13		0.43
Dioxane	11.82	11.94	12.06		12.18	12.30	12.42	12.62	12.84
DME	11.77	11.89	11.99		12.12	12.25	12.37		0.67
Me ₂ SO	11.76	11.88	12.06		12.24	12.42	12.61	12.99	13.32

^a ΔpH is the difference of the pH at $\phi = 0.30$ and the pH at $\phi = 0.0$ i.e., 11.7.

monitoring the formation of the *p*-nitrophenol was 410 nm. All the rate constants are accurate to within ± 5 –8% except in cases when the substrate molecules are aggregating. In these cases the kinetics deviate from first-order, hence the pseudo-first order rate constants were obtained from the linear portion of the curves for the initial stage of the reaction (Murakami *et al* 1974; Jiang *et al* 1984), and the experimental uncertainties are around $\pm 10\%$.

3. Results

A total of four hundred and eighty-six pseudo-first-order rate constants (k_{ob}) of the hydrolysis of C2, C8, C12 and C16 in six aquiorgano binary mixtures of graded compositions (ϕ) at various initial substrate concentrations ([S]) are listed in tables 2, 3, 4 and 5, respectively.

4. Discussion

For solvent effect studies, the direct comparison of hydrolytic rate constants of a short-chain ester with those of a long-chain ester will become hardly meaningful if the latter type of substrate begins to aggregate. Previous results have indicated that the hydrolysis of long-chain esters in aggregating solvents is an exceedingly complicated process, and the relative importance of the various paths leading to the product P from substrate S depicted in scheme 1, i.e., k_m , k_{agg} , k_{coil} , may change greatly under different conditions. (Jiang *et al* 1984, 1985; Fan and Jiang 1985).

Table 2. Rate constants, k_{ob} (10^{-2} s^{-1}), of the hydrolysis of C2 in various aquiorgano solvents at different initial [S] (10^{-5} M) and ϕ values.

Organic cosolvent	ϕ	Initial [S], 10^{-5} M			Organic cosolvent	ϕ	Initial [S], 10^{-5} M		
		0.2	2.0	20			0.2	2.0	20
<i>n</i> -PrOH	0.00	8.71	8.62	8.62	DME	0.05	8.65	8.63	8.65
	0.05	8.36	8.27	8.36		0.10	8.75	8.68	8.71
	0.10	8.18	8.27	8.18		0.15	8.89	8.95	8.90
	0.15	8.18	8.07	8.07		0.20	9.05	9.13	8.99
	0.20	7.42	7.31	7.42		0.25	9.35	9.29	9.15
	0.25	6.32	6.30	6.27		0.30	9.60	9.48	9.25
	0.30	5.67	5.60	5.70					
<i>t</i> -BuOH					Dioxane	0.05	0.96	9.51	9.51
	0.05	8.33	8.33	8.33		0.10	10.4	10.3	10.3
	0.10	7.50	7.70	7.60		0.15	11.0	11.0	11.2
	0.15	6.90	6.93	6.87		0.20	12.0	12.1	12.0
	0.20	5.43	5.47	5.40		0.25	12.8	13.0	12.8
	0.25	4.60	4.69	4.53		0.30	13.2	13.2	13.2
	0.30	3.53	3.63	3.51	Me_2SO	0.15	14.3	14.5	
						0.25	19.0	19.5	

Table 3. Rate constants of the hydrolysis of C8, k_{obs} (10^{-3} s^{-1}) at 35°C.

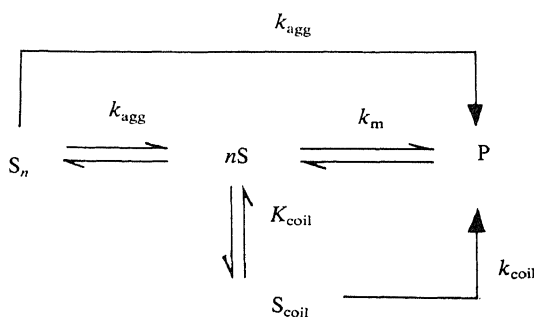
Organic cosolvent	ϕ	Initial $[S]$, 10^{-5} M													
		0.2	0.4	0.6	0.8	1.0	1.2	1.5	2.0	2.5	4.0	6.0	8.0	10.0	20.0
MeOH	0.00	48.5	50.4			49.1			29.0		13.3			5.2	
	0.05	88.9	88.9			89.3			63.3		34.1			12.0	
	0.10	133	133			136			120		94.7			31.7	
	0.20	183	183			185			181		173			91.1	
<i>n</i> -PrOH	0.05	44.9				44.0	43.7		35.0		18.0			6.8	
	0.10	39.1							39.3	38.7	27.3	17.8		10.9	
	0.15	30.7				30.0			21.0		31.0	30.5	30.5	26.1	
	0.20	20.8													21.3
	0.25	18.0				18.3									17.9
	0.30	16.0							16.0						15.7
<i>t</i> -BuOH	0.05	42.3				41.3	40.7	38.3	28.3		14.9			5.4	
	0.10	34.6		41.3		34.5		34.5	33.3		18.0			6.9	3.6
	0.15	23.7				24.3			24.0		23.3	21.1		13.3	
	0.20	13.1							13.1						12.8
	0.25	8.6							8.7						8.7
	0.30	6.6							6.5						6.7
DME	0.05		43.0			43.0			31.1		16.0			6.1	
	0.10		40.0						40.3		22.0			8.6	
	0.15		37.4						37.3		35.5	21.0		13.0	
	0.20		34.3								34.0	31.7		16.1	
	0.25		33.3						32.9			32.7	32.7	31.3	
	0.30		32.7						33.0			32.0			
Dioxane	0.05		51.3		50.2	50.4			45.6		22.7			8.5	
	0.10		51.8			51.1			50.7		47.1			17.6	
	0.15		51.6			51.6			51.0		50.7	48.0		30.3	
	0.20		51.0			51.0					51.0	49.8		47.6	29.3
	0.25		50.9						50.7				50.7	49.0	41.0
	0.30		51.8											50.2	45.7
Me ₂ SO	0.15		59.6			60.4			59.6		43.1	26.7		15.7	
	0.30		72.0			71.1			70.2		70.2	67.6		42.7	
	0.45		87.1			88.0					85.3			86.2	

Table 4. Rate constants of the hydrolysis of C12, k_{ob} (10^{-3} s^{-1}) at 35°C.

Organic component of solvent	ϕ	Initial [S], 10^{-5} M												
		0.2	0.3	0.35	0.40	0.6	0.8	1.0	2.0	4.0	6.0	8.0	10.0	20.0
MeOH	0.20	75.0			37.0			10.4	4.37	2.0			1.0	
	0.25	137	137	116	70.8	52.0		28.7	11.7	5.0			1.87	
	0.30	165				167	153	79.2	43.3	20.2				
<i>n</i> -PrOH	0.05	2.6			1.11			0.49	0.25					
	0.10	6.8			3.10			1.20	0.58	0.31				
	0.15	28.4			20.2	12.7		7.7	4.1	2.1			0.90	
	0.175	25.0	26.1		25.0	24.7		23.7	13.3	6.80			2.62	
	0.20	22.4						22.0	21.7	21.7	17.8		10.7	6.1
	0.25	18.3							18.0		18.2		18.0	17.8
	0.30	15.6							15.5					15.3
<i>t</i> -BuOH	0.05	1.5			0.75	0.51		0.31	0.21					
	0.10	2.4			1.15	0.80		0.46	0.28	0.16				
	0.15	13.4			8.9	6.1	4.6	3.8	1.90	1.10				
	0.175	12.5	12.1		12.5	12.5	12.3	11.6	7.3	3.6	2.7		1.6	0.8
	0.20	10.3			10.3			10.3	10.3	9.8	7.1	6.0	4.6	2.3
	0.25	7.1							7.0					7.0
	0.30	5.5							5.5					5.7
DME	0.15	9.2			4.5			1.7	0.75					
	0.20	20.2			9.8			3.17	1.47					
	0.25	30.6			22.7			8.13	3.60					
Dioxane	0.30	30.5			30.4			24.0	11.0	4.92			2.0	
	0.10	5.3			2.5	1.6		0.95	0.49					
	0.15	12.0			6.0			2.27	1.00					
	0.175	19.0			10.2	6.0		3.73	1.7	0.93				
	0.20	24.2			14.4	9.4		5.00	2.9					
Me ₂ SO	0.25	24.8			25.2	24.9	21.8	16.8	7.5	4.0			1.58	
	0.30	23.3			24.0	24.2		23.1	21.1	10.8			3.93	
	0.15	5.07			2.60	1.78		1.10	0.60					0.54
	0.30	28.0			15.3	11.3		7.0	3.42	1.67				

Table 5. Rate constants of the hydrolysis of C16, k_{ob} (10^{-3} s^{-1}).

Organic cosolvent	Initial [S], 10^{-5} M									
	ϕ	0.2	0.4	0.6	0.8	1.0	2.0	4.0	6.0	10.0
<i>t</i> -BuOH	0.15	0.97	0.55	0.34		0.23	0.19			
	0.175	5.5	2.9	2.1		1.25	0.83	0.475		
	0.20	9.6	9.6	8.3		6.0	3.0	1.48		0.64
	0.25	7.3				7.3	7.3	7.2	6.6	4.4
	0.30	5.4	5.5					5.5		5.5
<i>n</i> -PrOH	0.15	5.8	2.7			0.92	0.68	0.35		0.34
	0.20	21.3	21.9	21.9	19.7	14.3	7.3	3.6		1.4
	0.25	18.7					18.7		18.9	13.7
	0.30		15.3				15.5			
DME	0.30	5.2	2.4			0.89				
Dioxane	0.20	0.94	0.51			0.20	0.14			
	0.30	7.5	3.40			1.30	0.62	0.29		0.18
	0.40	16.2	15.9			14.2	6.4	3.4		1.25
Me ₂ SO	0.20	0.18	0.10			0.08	0.07			
	0.40	1.46	0.76			0.38	0.22	0.16		
	0.50	9.8	5.4			2.21	1.15	0.64		0.27

**Scheme I**

Fortunately, we can usually get around such complications by measuring the rate constants of the "monomeric" forms from $\log k$ vs. initial $[S]$ plots as exemplified by the curves in figure 1. If the solvent is not too strongly aggregating, then there will be a plateau region in which k_{ob} is independent of the initial $[S]$, this k_{ob} is generally accepted as the rate constant of the monomeric ester (Guthrie 1973; Murakami *et al* 1977; Jiang *et al* 1984; Menger and Venkataram 1986). Another important feature of these curves is the break-points after which the k_{ob} values decrease with increasing $[S]$. In analogy to the CMC of micelle chemistry we can designate them as the critical aggregate concentrations, or CAgC, and a discussion of our CAgC values tabulated in tables 6 and 7 will be presented later. Incidentally, the k_{ob} values of C2 are always independent of $[S]$ (table 2).

Table 6. CAgC values for C8 in various aquiorcano mixtures.

Organic cosolvent	CAgC (10^{-5} M)							
	$\phi =$	0.0	0.05	0.10	0.15	0.20	0.25	0.30
<i>n</i> -PrOH		1.0	1.6	2.9	8.3	>10		
<i>t</i> -BuOH			1.5	2.2	5.5	>10		
Dioxane			1.7	3.6	6.2	>10	>10	
DME			1.4	2.0	3.6	7.2	>10	
Me ₂ SO					2.8			5.9
MeOH			1.3	2.6		5.3		

Table 7. CAgC values for C12 in various aquiorcano mixtures.

Organic cosolvent	CAgC (10^{-5} M)							
	$\phi =$	0.00	0.10	0.15	0.175	0.20	0.25	0.30
<i>n</i> -PrOH		<0.2	<0.2	0.28	1.0	5.0	>10	
<i>t</i> -BuOH			<0.2	0.26	1.0	4.2	>10	
Dioxane						<0.2	0.63	1.8
DME						<0.2	0.26	0.74
Me ₂ SO								<0.2
MeOH						<0.2	0.30	0.66

For each substrate and solvent a figure with curves corresponding to different ϕ 's can be obtained, as exemplified by figure 1. Whenever there is a break-point in these curves, a CAgC value can be determined, and with these CAgC values (tables 6, 7) one can judge which k_{ob} can be used as rate constants for monomeric substrates.

Although a number of factors will influence the magnitude of the k_{ob} , e.g., pH, H-bonding, or other solvent polarity properties, these will tend to remain relatively unchanged when different esters are compared in the same medium. This has allowed us to show the contributions of lipophilic forces, i.e., lipophilic solvation of the esters by the organic solvent molecules, by the following approach.

For each substrate, a figure consisting of $\log k$ vs. ϕ curves corresponding to different solvent systems is drawn, i.e., figure 2 for C2, figure 3 for C8 and figure 4 for C12, (the curves for Me₂SO and DME are missing because C12 aggregates at these ϕ values; for the same reason, the MeOH, Me₂SO, DME, dioxane curves cannot be constructed for C16), then (1) the different curves for different solvents in the same figure, and (2) the different trends of these curves in different figures for short and long substrates, are compared and analysed.

Several interesting and significant observations will stand out by following the aforementioned approach (for somewhat related observations, see Elsemongy *et al* 1981, Singh *et al* 1981, Yang and Fagley 1981, Engberts 1982): (1) There are three types of solvents, Me₂SO and MeOH increase the rates with increasing ϕ , *n*-PrOH and *t*-BuOH decrease the rates with increasing ϕ , dioxane and DME are in

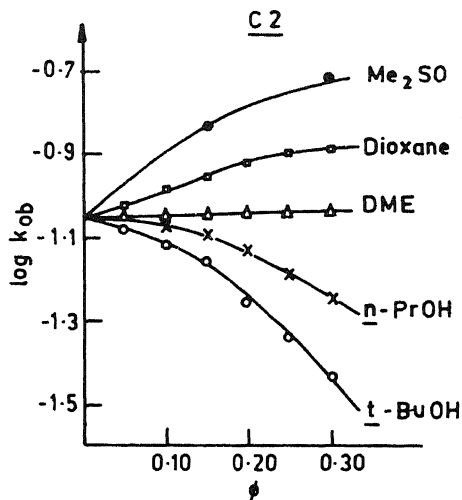


Figure 2. $\log k_{ob}$ vs ϕ plots for C2 in different aquiorgano solvents.

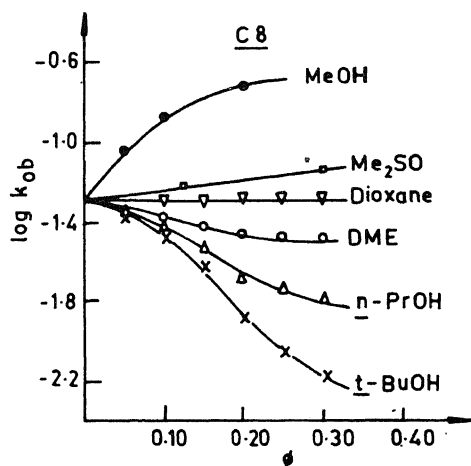


Figure 3. $\log k_{ob}$ vs ϕ plots for monomeric C8 in different aquiorgano solvents.

between. With increasing ϕ , dioxane increases the rates of C2 but has little effect on those of C8, whereas DME has little effect on the rates of C2 but decreases the rates of C8 to some extent. (2) A comparison of the trends or "slopes" of all the curves for C8 and C12 (figures 3 and 4) with those for C2 (figure 2) will show a very intriguing feature: all the curves for C2 seem to have been "pushed down" by some "force" when they reappear in figures 3 and 4. Why?

On the basis of our propositions previously stated, we rationalize our results in terms of the following reasonings or speculations (designated later as points 1, 2 etc.).

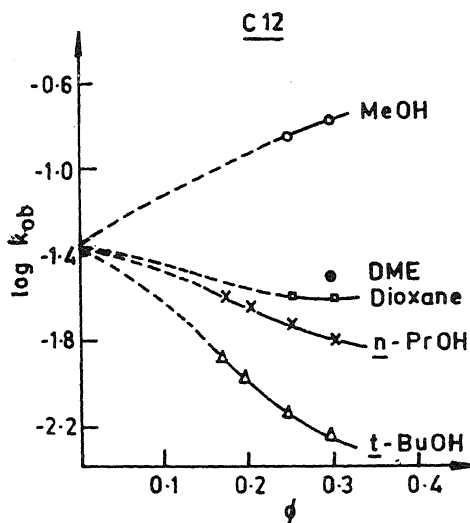
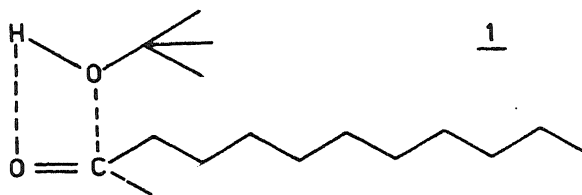


Figure 4. Log k_{ob} vs ϕ plots for monomeric C12 in different aquiorcano solvents.

1. Solvation of ^-OH through H-bonding by the solvent molecules is in the order: protic > aprotic; and for the protic solvents: $H_2O > MeOH > i\text{-}PrOH, t\text{-}BuOH$. Since the solvating abilities of water and the cosolvents should also be related to the acceptor numbers AN (Gutmann 1978; Reichardt 1979), which are 54.8 for H_2O , 41.3 for MeOH, 37.1 for EtOH and 33.5 for *i*-PrOH. Thus the factor of desolvation of OH^- upon adding more organic cosolvent alone will tend to increase the rates in varying degrees for all organic cosolvents, and more so for the aprotic ones. (AN values: Me_2SO 20.4, dioxane 10.8, DME 10.2). The fact, however, is that only some of them accelerate the rates. And, in our judgement, the most important conclusion that can be deduced from this fact is: the conspicuous retarding (instead of accelerating) effects of adding more *n*-PrOH and *t*-BuOH are necessarily consequences of the operation of another opposing force.
2. The opposing force most likely originates from lipophilic interactions between organic cosolvent molecules and the esters, including C2 which also possesses a phenyl group. These interactions will lead to the well-known phenomenon of heteroselective solvation (Reichardt 1979) of substrate molecules by organic cosolvent molecules and thus retarded rates.
3. The magnitude of the above mentioned lipophilic heteroselective solvation effect on C8 should be larger than that of C2. Thus a crucial test of the credibility of our proposition (point 2) is whether this expectation has been borne out by fact. The fact is: everyone of the five curves in figure 2 is "pushed down" in figure 3, it could hardly be a consequence of fortuity.
4. Another possibility exists, especially when *n*-PrOH and *t*-BuOH are the cosolvents, namely, specific solvation involving "complexes" such as 1, which can also be looked upon as encounter pairs with longer lives than those involving smaller molecules. In these complexes H-bonding and polar interactions together will tend to hold the polar parts of the ester and cosolvent molecules together,



whereas lipophilic interactions will try to pull the hydrocarbon moieties together. Certainly, larger organic fragments of either partner of the complex will tend to increase the magnitude of this specific solvation effect (cf. MH values which reflect the lipophilicity of the alkyl groups, Menger, 1986).

5. The desolvation and increased activity of the ^-OH brought about by the addition of organic cosolvents is reflected in the increased pH values which can be arbitrarily measured by ΔpH values defined as the difference of pH at $\phi = 0.30$ and pH at $\phi = 0.00$. The tabulated ΔpH values make the last column of table 1 the most noteworthy column. Evidently the trend of these ΔpH values are in complete harmony with discussions presented in point 1. Of course, the higher cation solvation ability of Me_2SO (Parker 1969) may also contribute to the exceptionally high ΔpH value for Me_2SO .

6. The somewhat peculiar behavior of $MeOH$ is manifested by both its exceptional ability to accelerate the hydrolytic rate (figures 3 and 4) and its unusually low ΔpH value. This is very likely a consequence of the fact that the pK_a of $MeOH$ is 15.7–16, very close to the pK_a value of H_2O , i.e., 15.7 (Lowry 1982) (the pK_a 's of other alcohols have been reported to be >17). Thus a second and possibly more reactive nucleophile, $^-OCH_3$, may also be participating in the "hydrolysis" of the substrates.

7. Finally we have yet another piece of clear evidence for the existence of lipophilic interactions in solvent effects from the perspective of the applicability of Rekker's f constants (Rekker 1977; Rekker and de Kort 1979). Very recently, first examples of successful correlations of f constants with the deaggregating abilities of ten organic cosolvents (Jiang *et al* 1984) and hydrolytic rate constants of twelve substituted phenyl esters of *n*-hexadecanoates have been reported (Fan and Jiang 1985). The individual curves corresponding to the different cosolvents in figures 2, 3 and 4 all show the same ordering of their effects on the hydrolytic rates, viz., (on account of the facts already discussed in point 6, $MeOH$ is excluded from this ordering).

<i>t</i> -BuOH,	<i>n</i> -PrOH,	DME,	dioxane,	Me_2SO .
(0.37)	(0.34)	(-0.15)	(-0.42)	(-1.35)

Evidently this ordering is exactly the same as the ordering according to Rekker's Σf values shown in paranthesis. Thus lipophilic forces are doubtlessly involved in these solvent effects.

In support of the above arguments are the trends of the C_{AgC} values shown in tables 6 and 7. The C_{AgC} is a direct physical indicator of the deaggregating ability of an organic cosolvent, i.e., a larger value reflects a higher ability. Table 6 shows that at $\phi = 0.20$ for *n*-PrOH and *t*-BuOH, the C_{AgC} already can no longer be found in the range of substrate concentrations studied (i.e., no break-point appears

for the "plateau" line in this concentration range) the corresponding value for dioxane and DME is somewhere between 0.25 and 0.30, whereas in the $\phi = 0.30$ Me₂SO-H₂O system, C8 still aggregates easily. Therefore the order of deaggregating abilities derived from CAgC data again looks familiar, i.e., *n*-PrOH, *t*-BuOH > dioxane, DME > Me₂SO. From these observations we are tempted to conclude: The dynamic processes of lipophilic heteroselective solvation of monomeric organic substrates and deaggregation of the substrate aggregates by organic cosolvent molecules are in essence or in nature one and the same thing, although they may be looked upon as two processes. The actors under our spotlight are all interacting with lipophilic (as well as other important) forces.

It has been shown previously that in a particular medium, the k_{ob} of a nonaggregating shorter substrate divided by the k_{ob} of the monomeric form of an aggregating longer substrate gives a measure of the rate retarding effect of self-coiling of the longer substrate (Jiang *et al* 1984). The present work provides some additional data in terms of the k_8/k_{16} or k_8/k_{12} ratios listed in table 8. Evidently, there is practically no rate retardation brought about by self-coiling in *n*-PrOH, *t*-BuOH, and DME and a very small effect in dioxane. This ratio is not available for the Me₂SO system since aggregation occurs in the whole range of composition studied and no CAgC values can be obtained.

5. Conclusion

In the past it has not been easy to reveal the contributions to the total solvent effect from lipophilic interactions between organic cosolvent and substrate molecules in a relatively simple and straight forward manner, either because the substrates used were relatively small or because complicating factors such as aggregation made a direct comparison of long-chain substrates with short ones impossible. The present work makes this comparison possible by first finding out the CAgC values of the long-chain esters under specific conditions, then comparing the rate constants of the monomeric forms of octanoates, dodecanoates, hexadecanoates with those of

Table 8. The rate ratios k_8/k_{12} and k_8/k_{16} in various aquioorgano mixtures.

Organic cosolvent	ϕ	k_8/k_{12}	k_8/k_{16}
<i>n</i> -PrOH	0.20	1.0	1.0
	0.25	1.0	1.0
	0.30	1.0	1.0
<i>t</i> -BuOH	0.20	1.1	1.2
	0.25	1.1	1.0
	0.30	1.1	1.0
DME	0.25	1.1	
	0.30	1.1	
Dioxane	0.25	2.0	

the acetates. When such comparisons were made in six aquiorghano solvents the lipophilicity of which could be changed by either the nature or the content of the organic component, it became clear that lipophilic interactions were playing an important role in solvent effects of aqueous binaries.

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The effect of hydrophobic-lipophilic interactions on chemical reactivity. 10. The competition between the aggregation of long-chain esters and the formation of inclusion complexes of these esters with amylose

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Abstract. The hydrolytic pseudo-first-order rate constants (k_{ad}) of *p*-nitrophenyl esters of dodecanoic acid (C12) and hexadecanoic acid (C16) at different initial substrate concentrations ($[S]_0$) in the six aquiorghano binary mixtures of different compositions (ϕ) were measured. These rate constants (k_{ad}) were compared with the corresponding rate constants obtained in the absence of sodium carboxymethylamylose (Na-CMA) (k_{un}) in order to study the competition between the formation of inclusion complexes of these esters with Na-CMA and the aggregation of these long-chain substrates. Values of $\Delta CAgC$ and k_{ad}/k_{un} were compiled and their significance discussed on the basis of a postulated two-path mechanism. Our results suggest that in addition to path A which involves encapsulation by Na-CMA of the monomeric C12 or C16 only, there is a second path (path B). Path B describes a process in which Na-CMA breaks up aggregates of all sizes into smaller ones as well as monomeric species which can be wrapped-up by Na-CMA simultaneously or subsequently.

Keywords. Hydrophobic-lipophilic interactions; aggregation of long-chain esters; inclusion complexes; chemical reactivity.

1. Introduction

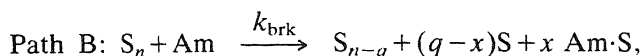
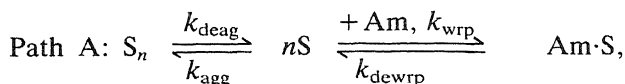
In aquiorghano or aqueous solutions in the presence of amylose or its derivative, sodium carboxymethylamylose (Na-CMA), the hydrophobic-lipophilic force acts on long-chain ester substrate molecules (S) as if with ambivalent intentions. On the one hand, it strives to loop them into hairpins, or better still, push them together and make them form aggregates (Menger and Portony 1968; Blyth and Knowles, 1971; Guthrie 1973; Murakami *et al* 1977; Jiang *et al* 1984, 1985; Menger and Venkataram 1986). On the other hand, it contrives to keep them single and straightened-up in the helical cavities of amylose or Na-CMA (Hui *et al* 1981; Cheng *et al* 1985; Jiang *et al* 1984). Thus the same force appears to lead to two competing processes. It also leads us to ask two questions. (1) Can the second process, the formation of inclusion complexes, compete or coexist with the first (aggregation)? (2) If it can, then how?

Our previous work has already demonstrated that in $\phi = 0.50$ or $50:50$ (v/v) Me_2SO-H_2O solutions, phenyl and para-substituted phenyl esters of hexadecanoates at concentrations ranging from 1×10^{-5} M to 5×10^{-5} M can form host-guest complexes with amylose (Hui *et al* 1982, 1984; Jiang *et al* 1984, 1985) while they are already involved in the reversible process of aggregation (k_{agg}) and de-aggregation (k_{deag}) (Jiang *et al* 1984). The same is true with dodecanoates and octanoates

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(Huang 1985). Therefore, in the sense that coexistence signifies the ability to compete, the first question has already been affirmatively answered, with the stipulation that such things happen either only in the aqueous solution or in certain aquiorghano mixtures within a narrow range of ϕ values (volume fractions of the organic cosolvent).

Scheme I



$$x \leq q; q < n.$$

We may now attempt to address the second problem, i.e., how does the second process compete with the first? Scheme I depicts two possibilities. (1) Path A: Amylose (Am) or Na-CMA (Am) can only wrap up monomeric S molecules (k_{wrp}) to form inclusion complexes $\text{Am} \cdot S$, whereas the monomeric species S are continuously formed from de-aggregation (k_{deag}) of the aggregates S_n (the subscript n stands for the degree of aggregation) which function as reservoirs of S. (2) Path B: Am somehow can perturb or break up S_n (k_{brk}) partially or wholly and encapsulate one or more "liberated" S molecules simultaneously or subsequently. A notable feature of this path is that it might lead to increased concentration of the monomeric species ([S]).

At the first glance, it appears extremely difficult to prove or disprove the reality of path B. For instance, although chemical intuition suggests that the weakly organized S_n can hardly withstand or completely survive a head-on collision with the giant Am molecule, one can always argue that the above-mentioned previous observations on hexadecanoates, dodecanoates and octanoates can be easily rationalized by path A alone, because k_{deag} should be very much larger than k_{wrp} , thus plenty of monomeric S are always constantly available from de-aggregation of S_n .

In fact, we took the last statement as a possible key which might help us solve this intriguing problem. In conformity with that statement we speculated that operation of two open paths (A+B) could more effectively increase the total amount of the monomeric species ($S + \text{Am} \cdot S$) than the operation of only path A could. Thus finding a way to measure the change in the concentration of the monomeric species upon addition of Am might shed light on our problem.

Fortunately we already have in our hands a tool which may prove to be useful for our purpose. The previous paper of this series (Part 9, Jiang *et al* 1987a) has discussed the significance and method of measuring the critical aggregate concentration, or CAgC (see also Guthrie 1973; Murakami *et al* 1977; Menger and Venkataram 1986; Jiang *et al* 1984), of these long-chain esters. The CAgC value can be obtained from a hydrolytic rate constant (k) versus initial substrate concentration ([S]₀) plot and is a measure of the highest possible concentration of the monomeric species in a particular aggregating medium, as exemplified by the

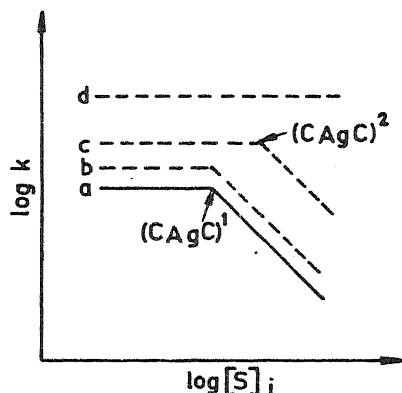


Figure 1. $\log k$ vs. $[S]_i$ plots for an aggregating medium. Effects of adding Am on the hydrolytic behavior of an ester S (cf. text).

$(CAgC)^1$ of curve (a) in figure 1. Indeed, on the basis of previously discussed propositions, even before experimentation one could make up or sketch out a scenario for possible events (pertinent to the viability of path B) that might occur after adding Am to a solution of an ester S in an aggregating medium (dashed lines in figures 1 and 2). In figure 1, the solid line (a) represents the hydrolytic behavior of a long-chain ester S in a particular aggregating medium in the absence of Am; its $CAgC$ is designated as $(CAgC)^1$. If Am is added, the $CAgC$ is designated as $(CAgC)^2$. Dashed-line (b) represents an event with $(CAgC)^2 = (CAgC)^1$, i.e., $\Delta CAgC = (CAgC)^2 - (CAgC)^1 = 0$, whereas line (c) depicts a case with $\Delta CAgC > 0$. Line (d) can be regarded as purely fictitious right at the beginning; it says that aggregates are completely annihilated by Am. Figure 2 shows the same plots in a highly aggregating medium, i.e., $(CAgC)^1$ cannot be found within the range of substrate concentration ($[S] \geq 2 \times 10^{-6}$ M) capable of being measured by the spectrometer. Lines a, b, and c bear the same meaning as their counterparts in figure 1.

The present work is therefore an effort at realizing or invalidating these expectations by studying dozens of these $\log k$ vs. $[S]_i$ plots derived from a large number of observed hydrolytic rate constants, designated as k_{un} for those measured in the absence of Am, and k_{ad} , in the presence of Am. The symbol (m) pertains to the monomeric state, and (ag), the aggregated state. Thus $k_{ad}(m)/k_{un}(m)$ represents the ratio of the rate constants in the presence of Am to that of the monomeric species in the absence of Am at a particular initial substrate concentration $[S]_i$. The significance of such ratios as well as the $\Delta CAgC$ values will be discussed after the experimental results are presented.

Six aqueous binaries of various compositions (ϕ) were used in this investigation, viz., MeOH-H₂O, EtOH-H₂O, *n*-PrOH-H₂O, *t*-BuOH-H₂O, dioxane (DX)-H₂O, and Me₂SO-H₂O. NaCMA (Am) of five different degrees of substitution (D.S.) were used, namely, D.S. = 0.00 (i.e. amylose), 0.12, 0.18, 0.24, and 0.29. The esters used as substrates (S) were the *p*-nitrophenyl esters of dodecanoic acid (C12) and hexadecanoic acid (C16). N-Dodecanyl-3-acetoxypyridinium iodide, designated as 1, was also used as a substrate.

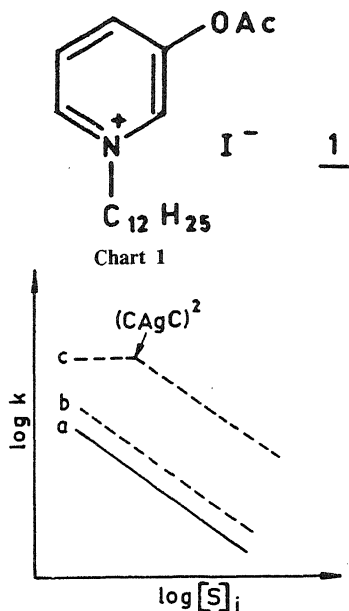


Figure 2. $\log k$ vs. $[S]_i$ plots for an highly aggregating medium. Effects of adding Am on the hydrolytic behavior of an ester S (cf. text).

2. Experimental

Substrates: Para-nitrophenyl dodecanoate (C12) and hexadecanoate (C16) and N-dodecanyl-3-acetoxypyridinium iodide (**1**) were prepared by methods reported previously (Jiang *et al* 1984; Hui *et al* 1983).

Amylose and sodium carboxymethylamylose: The amylose used was purified by the procedure previously described (Hui *et al* 1983). Sodium carboxymethyl amylose (Na-CMA), with different degrees of substitution by the $-CH_2CO_2Na$ group, was prepared by reactions of amylose with various amounts of chloroacetic acid and sodium hydroxide in 40:60 ethanol-water mixtures (Huang 1985). The degree of substitution for Na-CMA (abbreviated as ΓS) is defined as the number of carboxymethyl groups contained in each anhydroglucose unit.

Kinetics: The kinetic measurements of k_{ad} were carried out under identical conditions as described in part 9, except that buffer solutions containing 2×10^{-4} M of pre-dissolved amylose or Na-CMA were used. Rate constants measured in the absence of Na-CMA were reported in the previous paper. The experimental uncertainties for k_{ad} are around 5–10%.

3. Results

The hydrolytic pseudo-first-order rate constants (k_{ad}) of C12 and C16 at different initial substrate concentrations ($[S]_i$) in the presence of 2×10^{-4} M Na-CMA in six aquiorghano binary mixtures of different compositions (ϕ) are listed in tables 1 and

Table 1. Hydrolytic pseudo-first-order rate constants (k_{ad} , 10^{-3} s^{-1}) of C12 at different initial concentrations ($[S]_i$) in the presence of $2 \times 10^{-4} \text{ M}$ Na-CMA (DS = 0.12) in six aquiorghano mixtures of various compositions (ϕ).

Organic cosolvent	ϕ	$[S]_i$, 10^{-5} M								
		0.2	0.4	0.6	0.8	1.0	2.0	4.0	6.0	10.0
MeOH	0.20	123	122	113		60.8	25.0	11.4		3.8
	0.25	153	151	153	123	93	39.2	14.6		5.4
	0.30	163	162	162		160	85	40.0		13.2
EtOH	0.20	116	117	91		52.5	27.0	12.0		4.2
	0.25	103	100	103		86	39.4	21.9		7.9
	0.30	74.2	74.7			74.7	66.7	32.1		10.4
<i>n</i> -PrOH	0.15	59.3	60.0	54.4		38.4	19.8	8.5		3.3
	0.175	34.3	35.0			34.8	26.3	11.7		4.7
	0.20	22.7	22.7			22.5	22.6	22.5	21.3	12.8
<i>t</i> -BuOH	0.15	35.6	39.1	34.0		20.3	12.0	7.1	5.2	3.9
	0.175	25.7	25.7	25.3		24.7	15.6	9.9	6.2	4.7
	0.20	13.8	13.7			13.8	13.8	12.8	11.3	7.1
	0.10 ^a	21.3	13.3	8.4		4.9	2.7	1.4		
	0.15 ^a	21.7	17.2	11.8		7.5	3.7			
	0.175 ^a	13.0	13.2	13.1		12.4	7.1	3.6		1.6
	0.20 ^a	9.8	9.8			9.9	9.6	8.8		4.0
	0.25 ^a	6.0	6.2	6.2		6.1		6.3		6.0
Dioxane	0.15	113	112	90		53.3	27.0	12.5		4.8
	0.30	51.7	52.0	52.2		52.5	51.1	26.3		12.7
Me ₂ SO	0.15	117	116			53.3	28.0	13.3		6.0
	0.30	183	183			185	85	44.2		15.8
	0.0 ^a	21.2	10.3	7.2		4.5	2.3			

^a In the presence of $2 \times 10^{-4} \text{ M}$ Na-CMA with DS = 0.24.**Table 2.** Hydrolytic pseudo-first-order rate constants (k_{ad} , 10^{-3} s^{-1}) of C16 at different initial concentrations ($[S]_i$) in the presence of $2 \times 10^{-4} \text{ M}$ Na-CMA in three aquiorghano mixtures of various compositions (ϕ).

Organic cosolvent	ϕ	D S of NaCMA	$[S]_i$, 10^{-5} M							
			0.2	0.4	0.6	1.0	2.0	4.0	6.0	10.0
<i>t</i> -BuOH	0.15		17.0	8.9	6.9	4.3	2.2	1.2		
	0.20	0.12	10.5	10.4	9.6	7.7	4.0	2.4		
	0.25		6.9			6.8	6.6	6.8	5.9	4.1
Dioxane	0.20	0.12	26.3	15.9	10.7	6.7	3.5	1.74		0.72
	0.40	0.12	21.3	21.3	21.0	19.0	11.5	5.9		2.5
Me ₂ SO	0.20	0.12	15.1	7.5	4.53	2.7	1.44			
	0.40	0.0	57.3	57.2	52.5	32.9	20.0	11.6		6.1
	0.40	0.12	72.0	45.8	30.1	20.9	10.4	5.2		2.6
	0.40	0.29	26.4	13.2	9.3	6.3	3.13	1.60		0.65
	0.50	0.0	79	78	78	79	53.3	29.3		12.1
	0.50	0.12	119	79	57.3	37.5	17.9	8.17		3.93

2, respectively. Corresponding rate constants measured in the absence of Na-CMA (k_{un}) have been reported in the previous paper of this issue. The logarithms of all these k (k_{ad} or k_{un}) have been plotted against $\log [S]_i$ to yield many figures, only one of which is given as an example (figure 3), since for each aquiorghano binary system a similar figure can be drawn. Figure 3 shows that the possible effects of adding Na-CMA as postulated in the introductory remarks (cf. figures 1 and 2) have been borne out by experimental data. The $(\text{CAgC})^2$ values, as defined in the introduction, are derived from the 239 rate constants (k_{ad}) tabulated in tables 1 and 2. The $(\text{CAgC})^1$ values are obtained from k_{un} data presented in part 9. Both of them, as well as their differences, ΔCAgC [$(\text{CAgC})^2 - (\text{CAgC})^1$], are presented in table 3. For C16, owing to much higher degrees of aggregation, only a few ΔCAgC values can be obtained under our experimental conditions. Since the CAgC values for substrate 1 cannot be precisely measured and the ΔCAgC of 1 appear to be roughly nil, they are not tabulated.

4. Discussion

In §1, we have already briefly proposed a second possible mode of competition between inclusion-complex formation and aggregation, as depicted symbolically by path B in the scheme. Since the aggregation number n is not an exact number but represents a certain condition-dependent distribution of numbers, the quotation-marked rate or equilibrium constants are merely conceptual abstractions. Although nothing quantitative can be deduced from such a scheme, it nevertheless may be qualitatively meaningful. To be more exact or specific, we presume that the existence of path A as the first mode of competition is a self-evident fact which requires no further discussion; but path B as a speculation needs some elaboration. We visualize that the perpetually moving and tumbling giant polymers Am (amylose or Na-CMA) are in constant collisions with aggregates (S_n) of all sizes.

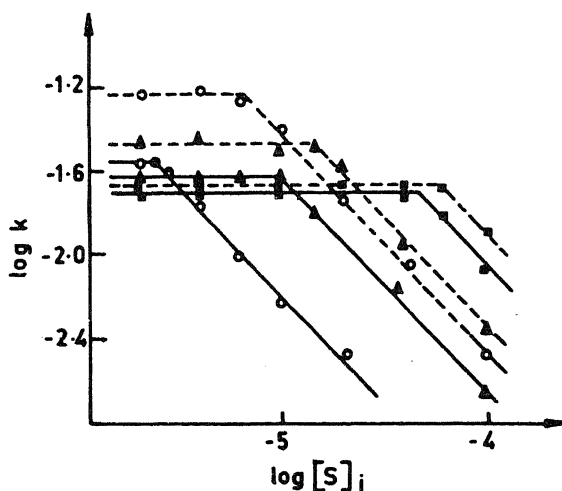


Figure 3. $\log k$ vs. $\log [S]_i$ plots for C12 in $n\text{-PrOH-H}_2\text{O}$ mixtures of different ϕ . $\circ$: $\phi = 0.15$; $\triangle$: $\phi = 0.175$; $\blacksquare$: $\phi = 0.20$; solid lines are for k_{un} ; dashed lines are for k_{ad} .

Table 3. (CAgC)¹, (CAgC)² and Δ CAgC values (10^{-5} M) for C12 and C16 in various aquioorgano mixtures.^a

Organic cosolvent	ϕ	C12			C16		
		(CAgC) ¹	(CAgC) ²	Δ CAgC	(CAgC) ¹	(CAgC) ²	Δ CAgC
MeOH	0.20	0.20	0.58	0.38~0.58			
	0.25	0.30	0.66	0.36			
	0.30	0.66	1.23	0.57			
EtOH	0.20	0.2	0.51	0.31~0.51			
	0.25	0.48	0.91	0.43			
	0.30	1.26	1.82	0.56			
n-PrOH	0.15	0.28	0.65	0.37			
	0.175	1.0	1.51	0.51			
	0.20	5.0	6.17	1.17			
tBuOH	0.15	0.26	0.32	0.12			
	0.175	1.0	0.98	-0.02			
	0.20	4.2	4.0	-0.2	0.60	0.72	0.12
Dioxane	0.15	0.2	0.48	0.28~0.48			
	0.30	1.8	2.29	0.49			
	0.40				0.83	1.1	0.27
Me ₂ SO	0.15	0.2	0.46	0.26~0.46			
	0.30	0.2	1.0	0.8~1.0			
	0.50				0.2	0.28	0.08~0.28
	0.50				0.2	1.38 ^b	1.18~1.38

^a The (CAgC)¹ values were reported in part 9. The (CAgC)² values are derived from the k_{ad} values measured in the presence of 2×10^{-4} M of Na-CMA (DS = 0.12) which are listed in tables 1 and 2.

^b Derived from k_{ad} values measured in the presence of 2×10^{-4} M of amylose (i.e. DS = 0)

Some of the "head-on" or forceful collisions may break an aggregate into one or more smaller aggregates (S_{n-q}) as well as one or more (q) monomeric species out of which one or more (x) monomers may be captured immediately or later on by Am as "guests" in Am·S. We further imagine that at initial substrate concentrations ($[S]_i$) fairly or very close to (CAgC)¹ small aggregates S_n may be easily broken into very small aggregates (S_{n-q}) plus some monomers or even completely into monomers (S), but at concentrations much higher than (CAgC)¹, although S_{n-q} species may still retain respectable sizes, some monomers or very small aggregates are bound to be simultaneously formed nevertheless. In other words, we believe path B is the most effective way to increase the concentration of the monomeric species (S + Am·S). To put it more bluntly, with Occam's razor in mind we suggest: any experimental observation of a positive Δ CAgC value under certain circumstances would make the existence of path B most likely.

A quick glance at table 3 may please those who agree with or can tolerate our speculations because most of the Δ CAgC listed are positive. Thus path B appears to be viable and realistic indeed. Naturally, things are much more complicated than has been said, and a closer scrutiny of the data (cf. tables 3 and 5) will further reveal other noteworthy and intriguing points.

Table 4. Hydrolytic pseudo-first-order rate constants, k_{ob} (10^{-3} s^{-1}), for 1 in pure water.

DS	Na-CMA conc. (10^{-4} M)	[S] _i , 10^{-5} M						
		1.0	2.0	4.0	8.0	10.0	20.0	40.0
	0	0.82	0.80	0.83	0.80	0.79	0.60	0.45
0.12	2.0	13.6	13.6	13.6	13.6	13.5	13.0	11.3
0.12	4.0	13.7	13.8	13.7	13.7	13.1	12.0	
0.18	2.0	9.65	9.61	9.6	9.5	8.61	7.18	

4.1 The ΔCAgC values

Table 3 reveals two outstanding facts: (1) Out of the twenty ΔCAgC (10^{-5} M) values, sixteen are positive and greater than about 0.15, the remaining four (-0.2 to 0.12) all belong to the *t*-BuOH system. (2) All the above mentioned sixteen ΔCAgC follow the same rule, they increase with increasing ϕ values for each of the five systems (MeOH, EtOH, *n*-PrOH, dioxane, Me_2SO). Let us address the second observation first.

Positive ΔCAgC values signify that in a particular system $(\text{CAgC})^2$ values increase more rapidly than $(\text{CAgC})^1$ when more of the organic component is added to that aqueous binary, whereas for negative ΔCAgC the reverse should be true. Since both inclusion-complex formation (k_{wrp}) and aggregation (k_{agg}) are driven by hydrophobic-lipophilic forces (both ΔG_{wrp} and ΔG_{agg} are negative), or in other words, increasing the lipophilicity of the medium should disfavor both of these two competing processes, i.e., increasing ϕ should favor both k_{dewrp} and k_{deag} (both ΔG_{dewrp} and ΔG_{deag} are positive) (Hui *et al* 1982; Jiang *et al* 1984, 1987), it does not seem immediately clear why we should have such a range of ΔCAgC , from values as high as $+1.3$ (Me_2SO , C16) to as low as -0.2 . Perhaps the following considerations are pertinent to this problem.

These two processes are both similar and dissimilar. They are similar in the sense that they are both consequences of hydrophobic interactions, but dissimilar because they may conform to different types of energetics. For instance, aggregation is favored by ΔS (Reichardt 1979) but encapsulation of uncharged esters by Am are disfavored by ΔS and favored by ΔH (Jiang *et al* 1985; Bender and Komiyama 1978; Murakami *et al* 1975), whereas complex formation of charged S species with Am is favored by both ΔS and ΔH (Hui *et al* 1981). In fact, our very recent work on both fluorocarbon and hydrocarbon substrates show that, in comparison with complex formation with cyclodextrins, encapsulation by Am may require additional help from lipophilic forces (Jiang *et al* 1987b). This state of affairs may be looked upon as a natural consequence of the fact that the structures and properties of the guest (S) and host (Am) are completely different, thus the general and specific solvent effects of the organic cosolvents on S and Am must be different (cf. part 9). These solvent effects surely depend on the nature of the organic cosolvent. Therefore, for each aquiorghano solvent system, the rate of free energy change (ΔG) with increasing ϕ should be different for these two competing processes, i.e., $d\Delta G_{\text{deag}}/d\phi$ and $d\Delta G_{\text{dewrp}}/d\phi$ are different, and naturally, the ΔCAgC values will vary accordingly.

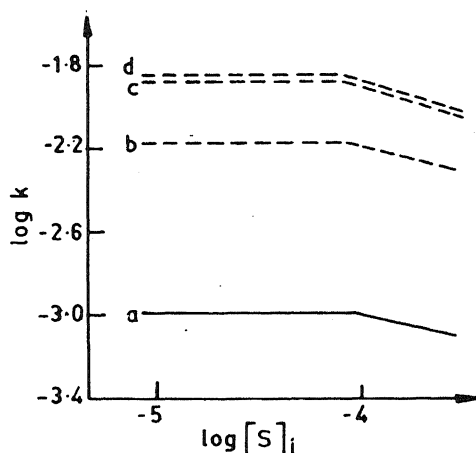


Figure 4. Log k_{obs} vs. log $[S]_i$ plots for 1 in pure water: a: in the absence of Na-CMA; b: in the presence of 2×10^{-4} M Na-CMA (DS = 0.18); c: in the presence of 2×10^{-4} M Na-CMA (DS = 0.12); d: in the presence of 4×10^{-4} M Na-CMA (DS = 0.12).

The sixteen positive ΔCagC values for the five solvent systems (vide supra) suggest that in these media $d\Delta G_{\text{deag}}/d\phi$ is larger than $d\Delta G_{\text{dewrp}}/d\phi$, i.e., upon adding more organic cosolvent, the substrate S loses its ability to aggregate faster than the host Am loses its ability to wrap up S. The lone exception thus far found is *t*-BuOH, the most lipophilic of all the six organics. It is hardly surprising if one remembers that it has acted just like that in a study involving ten aquiorghano systems (Jiang *et al* 1984). However, there is an additional message from the present work, it says: the properties of *t*-BuOH molecules are exceptionally well-adapted to solvate (thus stretch out) the Am molecules.

Finally, we want to present a particularly noteworthy piece of observation which has direct bearing on the credibility of path B. The preceding work (part 9) has established that among six cosolvents Me_2SO is least capable of increasing $(\text{CagC})^1$, yet the present work (cf. table 3) indicates that Me_2SO is the most capable of increasing ΔCagC ! In order to rationalize this interesting combination of facts, one would have to postulate then that k_{wrp} (or the hydrophobic-lipophilic interactions between Am and S) would be favored by increasing ϕ if path A alone were operating. This sounds unreasonable, thus we cast another vote of confidence for path B.

The behavior of the pyridinium compound 1 deserves some comments. Being positively charged and thus more hydrophilic, it barely shows some tendency to aggregate. This is not unexpected since it has been known that 16-CO_2^- is the maverick among six 16-Y substrates (when $\text{Y} = \text{H}, \text{NO}_2, \text{Cl}, \text{CH}_3, \text{OCH}_3$, aggregation observed, Jiang *et al* 1984). Nevertheless, it is noteworthy that the approximate CagC of 1 is still much smaller than the CMC values of charged surfactants. Thus 1 may be a member of those compounds whose behavior lies in-between neutral compounds which form aggregates and charged compounds which form micelles. We believe CagC values are normally several orders of magnitude smaller than CMC values. This difference might be used to differentiate between the two types of molecular assemblies.

4.2 The k_{ad}/k_{un} ratios

The ratios of the rate constants measured in the presence and absence of Am, listed as k_{ad}/k_{un} values in table 5, also deserve our attention. Previous work has established that our observed k_{ad} are catalyzed-hydrolysis rate constants of monomeric substrate species inside the helical cavities of Am. (Hui *et al* 1982, 1983; Jiang *et al* 1985; Huang 1985). Thus higher k_{ad}/k_{un} values signify both higher catalytic efficiencies and higher association constants ($K_a = 1/K_d$) of the inclusion complexes. Data compiled in table 5 reveal two interesting aspects. First, the $k_{ad}(m)/k_{un}(m)$ values obtained from the monomeric region for all six solvents are almost always smaller than the average $k_{ad}(ag)/k_{un}(ag)$ values obtained from the aggregate region. This fact is certainly in harmony with the proposition that path B is in operation. Secondly, all these ratios decrease with increasing ϕ . Clearly, this is

Table 5. The $k_{ad}(m)/k_{un}(m)$ and average $k_{ad}(ag)/k_{un}(ag)$ values for the hydrolysis of C12 and C16 in various binary mixtures.

Organic cosolvent	ϕ	Na-CMA ^a DS	for C12		for C16	
			$k_{ad}(m)$	$k_{ad}(ag)$	$k_{ad}(m)$	$k_{ad}(ag)$
			$k_{un}(m)$	$k_{un}(ag)$	$k_{un}(m)$	$k_{un}(ag)$
MeOH	0.0	0.24		15.4		
	0.20	0.12		5.8		
	0.25	0.12	1.1	3.3		
	0.30	0.12	1.0	2.0		
EtOH	0.20	0.12		11.5		
	0.25	0.12	2.9	6.8		
	0.3	0.12	1.8	2.6		
	0.3	0.18	1.5	1.7		
<i>n</i> -PrOH	0.15	0.12	2.1	4.5		
	0.175	0.12	1.4	1.8		
	0.20	0.12	1.0	1.2		
<i>t</i> -BuOH	0.15	0.12	3.4	5.6		18.5
	0.175	0.12	2.1	2.5		
	0.20	0.12	1.3	1.8		
	0.25	0.12			1.1	1.7
	0.10	0.24		10.5	0.95	0.93
	0.15	0.24	1.6	2.0		
	0.175	0.24	1.0	1.0		
	0.20	0.24	1.0	0.9		
Dioxane	0.15	0.12		23.5		
	0.20	0.12				34.0
	0.30	0.12	2.2	3.2		
	0.40	0.12			1.3	1.8
Me ₂ SO	0.15	0.12		45.5		
	0.30	0.12		25.6		
	0.40	0.12				55
	0.50	0.12				15.5
	0.40	0.29				17.5
	0.40	0.00				90

^a The concentration of Na-CMA was 2×10^{-4} M.

a reflection of the fact that the association constants or the tendency (or driving force) of the inclusion-complex formation are unfavorably affected by larger amounts of the organic cosolvent.

Notably, among the organic cosolvents studied, Me₂SO possesses the least ability to de-aggregate (lowest CAgC values, cf. part 9), yet it is one of the most capable to increase Δ CAgC and it also gives the highest $k_{ad}(ag)/k_{un}(ag)$ ratios. Thus Me₂SO can provide the widest range of composition (ϕ) for the study of the two competing processes, and the previous use of Me₂SO-H₂O as the medium was a fortunate choice which led, among other results, to the first successful application of Rekker's hydrophobicity-lipophilicity constants to the correlation analysis with rate constants (Fan and Jiang 1985; Huang 1985).

5. Conclusion

Hydrophobic-lipophilic interactions, together with Nature's other forces, lead to the creation of the most complicated and wonderful things, such as vesicles, cells and life. Aggregation and self-coiling may be one of the simplest ways in which hydrophobic-lipophilic forces manifest themselves since even micelle formations usually involve interactions among electrically charged species. The host-guest interactions of the flexible linear polymers amylose and Na-CMA with straight-chain substrates are also expressions of hydrophobicity-lipophilicity, except that here lipophilic interactions between the host and guest may also contribute to this process which in a sense mimics the induced-fit of enzymes. By now it can be said affirmatively that these two processes can coexist or effectively compete with each other. Furthermore, our data suggest that there are more than one pathways for them to compete (cf. scheme I), and that the big Am molecules can smash the larger aggregates into smaller pieces as well as monomeric ones. The role of the organic cosolvent, including their varying solvation effects on S, S_n, Am, and Am-S, is both important and interesting. Although all of them disfavor both aggregation and inclusion-complex formation, their abilities to do so differ. In fact, trying to understand more about the pertinent intrinsic properties of these and other organic solvents remains a challenge. Such understanding may very well lead to practical applications. Like the CMC in micelle chemistry, the CAgC may prove to be a useful tool in the study of aggregation and inclusion-complex formation in the future. All in all, however, we are just beginning to understand a little, and only in a simplistic and qualitative way, about these intriguing, complicated and often puzzling phenomena, and we believe other interested workers will develop some new weaponry for further and much improved studies of these phenomena.

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Association models for alcohol-water mixtures

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Abstract. Alcohol-water mixtures are often used as model systems for the study of hydrophobic interactions. In this respect, their thermodynamic properties are of particular interest since precise data are available over the whole miscibility range and they lend themselves readily to theoretical modelling. Three association models have been used to fit the volume data taken from the literature for aqueous methanol, ethanol and n-propanol at various temperatures. A simple micellization equilibrium explains the general trends but fails to fit the reduced excess volumes at both ends of the mole fraction scale. Better fits are obtained if interaction parameters are introduced, but these two parameters cannot easily be rationalized. A double association model (one for the alcohol and one for the water) gives the best fit and all the parameters have a physical significance. However, the parameters extracted, e.g. aggregation numbers, and their trends with temperature are not always realistic. Despite their limitations, these models illustrate well with the kind of avenues that can be explored to fit and interpret the experimental data of these complex systems.

Keywords. Chemical equilibrium model; water-alcohol mixtures; double association; aggregation number; binary mixtures.

1. Introduction

Alcohols are probably the most well-known solutes used for the study of hydrophobic effects, in view of their simple molecular structure, increasing hydrophobic character with chain length and high solubility in water. Most of their physical properties have been studied extensively over the years (Franks and Desnoyers 1985). Near infinite dilution, authors generally agree on the existence of a hydrophobic cosphere around the aliphatic chain which has some resemblance to clathrate hydrates, and this hydrophobic hydration increases with chain length. As the concentration increases, hydrophobic pair and higher order interactions occur between two or more alcohol molecules, and there is strong evidence that, in these complexes, the alcohol molecules are separated by a water molecule, somewhat as suggested by Iwasaki and coworkers (Iwasaki *et al* 1976; Iwasaki and Fujiyama 1977, 1979). As still higher concentrations, these structures collapse and clusters of alcohol molecules are formed which largely have the properties of pure alcohols.

Thermodynamic properties are of particular interest for the study of hydrophobic effects since they lend themselves readily to theoretical modelling (Desnoyers and Jolicoeur 1982). The infinite dilution partial molar quantities are functions only of the intrinsic properties of the alcohol and of the solute-solvent interactions. The

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initial slope in the concentration dependence of the partial or apparent molar quantities can be interpreted in terms of hydrophobic interactions between pairs of solutes (Kozak *et al* 1968; Okasaki *et al* 1984; Tanaka *et al* 1984). The high concentration data are more difficult to model in view of the complexity of the system. Eventually, theoretical models based on molecular dynamics or Monte Carlo calculations should succeed in reproducing the thermodynamic properties over the whole miscibility range, but at present the Kirkwood-Buff theory is about the only one that has been applied with some success (Donkersloot 1979). However, at our present state of knowledge, it is difficult to interpret the Kirkwood-Buff integral in terms of molecular interactions. To gain some understanding of the prevailing structures in these high concentration alcohol solutions therefore, simple chemical models, which are easy to treat mathematically, must be used. From these models, some information can in principle be gained from the magnitude of the parameters used to fit the data. The present paper will be concerned with some of these models which are analogous to a micellization process. The application will be limited to volumes since this where more accurate data exist, especially in the dilute regions.

2. Chemical models

The thermodynamic properties of liquid mixtures are often fitted with a polynomial equation. This approach is not satisfactory for strong interacting systems such as alcohol-water mixtures. For example, Benson and Kiyohara (1980) required up to 11 parameters of a power series to reproduce the thermodynamic functions of mixing of lower alcohol and water over the whole mole fraction range, and these parameters had no physical significance. It is therefore necessary to use models that are sufficiently simple to be handled mathematically and at the same time have some resemblance to the actual structure of the system. Such approaches have been proposed by many authors and in particular by Andreae *et al* (1965), Mikhailov (1968), Mikhailov and Ponomareva (1968), Iwasaki *et al* (1976), Iwasaki and Fujiyama (1977, 1979), Hvidt (1978), and Dethlefsen *et al* (1984). None of these models are at present entirely satisfactory.

A clue to the structure of alcohol-water mixtures is provided by the concentration trends of the thermodynamic properties. All properties undergo large changes over a relatively narrow concentration range. The sharpness of the transition region increases and the concentration domain for the change decreases as the chain length of the alcohol increases. The limited solubility in water prevents us from examining these trends beyond *n*-propanol for the linear alcohols and *t*-butanol for the branched ones. *n*-butanol can be made completely miscible with water by the addition of a small quantity of surfactant (Roux-Desgranges *et al* 1982). The miscibility barrier can also be overcome by increasing the hydrophilic character of the polar group. This can be done by the addition of ethoxy groups on the chain or by replacing the $-OH$ group by an amine or a phosphine oxide. In such cases, the thermodynamic properties of the solutes change gradually with chain length. For example, in the case of alkyltrimethylamine oxides (Desnoyers *et al* 1982), the lower members of the series are quite similar to alcohols while the long-chain homologs are typical nonionic surfactants. Also, the study of ternary systems of

water-alcohol-hydrocarbon (Smith *et al* 1977; Keiser *et al* 1979; Lara *et al* 1981) strongly suggests that alcohols exist as microaggregates into which the hydrocarbons dissolve preferentially. Therefore, in these organic-water mixtures, microphases of alcohols or of other similar solutes exist in a form that has similarities with micelles. In fact, a mass-action model (Desnoyers *et al* 1983), which was developed for non-ionic surfactants, can be applied to alcohol-water mixtures (Roux *et al* 1984), and the aggregation numbers extracted are of the order of 4 to 7 which is not unreasonable. Unfortunately, this model, which had been developed with the dilute solution approximation, cannot be applied as such to high concentration data. This model will presently be extended to cover the whole mole fraction range.

3. Single equilibrium ideal model

Successful models should apply to all properties, involve a minimum number of adjustable parameters which have some physical significance and reproduce precisely the experimental data. The simplest approach is therefore to identify the equilibrium processes best-suited for alcohol-water mixtures.

The chemical models for micellar systems fall into two main groups (Desnoyers *et al* 1986). The pseudo-phase models assume that the surfactant exists as monomers up to a critical micellar concentration which is equivalent to a monomer solubility. Beyond this CMC, the added surfactant will aggregate to form micelles. These simple models are appropriate for long-chain-surfactants that have a relatively sharp CMC region. With shorter-chain surfactants, the mass-action models, which assume an equilibrium between monomers and aggregates of a finite size, are preferable. In the simpler case, micellization is assumed to occur in a single step, i.e., for monodispersed micelles:



where a is the aggregation number of the micelles M in equilibrium with the monomers. Since the properties of the surfactant in the monomeric and micellar regions are different, these species will be identified as A and A' .

In the most simple micellar model, alcohols in water are assumed to form an ideal associated solution (Prigogine and Defay 1950). The solution is thus considered a mixture of monomers, association complexes and water, each species behaving ideally. The chemical potential of each species is given in the mole fraction scale by:

$$\mu_i = \mu_i^0 + RT \ln X_i, \quad (2)$$

where the standard state is the pure liquid of each species. Following the usual convention, the solvent is denoted as component 1, while the solute is the component 2, which can exist in the form A or A' . If n_i is the number of particles of each species, then the fraction of alcohol in the monomeric form is given by:

$$\alpha = n_A/n_2. \quad (3)$$

The number of aggregates in solution are then:

$$n_M = n_2(1 - \alpha)/a. \quad (4)$$

To simplify the notation, the fraction D is defined as:

$$D = \sum_i n_i / (n_1 + n_2) = X_2[\alpha + (1 - \alpha)/a] + X_1. \quad (5)$$

Under these conditions, the total Gibbs free energy of the system is given by:

$$\begin{aligned} G/RT &= \sum_i n_i \mu_i / RT = n_2 \alpha [\mu_A^0 / RT + \ln((\alpha X_2 / D))] + \\ & (n_2(1 - \alpha)/a) \{ \mu_M^0 / RT + \ln[(1 - \alpha)X_2 / aD] \} + \\ & n_1 [\mu_1^0 / RT + \ln(X_1 / D)]. \end{aligned} \quad (6)$$

The equilibrium condition for this system is:

$$\begin{aligned} [\partial(G/RT)/\partial\alpha]_{T,P,n_1,n_2} &= 0 \\ &= n_2 \{ [\mu_A^0 / RT + \ln(\alpha X_2 / D)] - (1/a) [\mu_M^0 / RT + \ln((1 - \alpha)X_2 / aD)] \}, \end{aligned} \quad (7)$$

which can be rewritten as:

$$\begin{aligned} (\mu_A^0 - \mu_M^0/a) / RT &= (\mu_A^0 - \mu_A^0) / RT = -\Delta\mu_A / RT \\ &= (1/a) \ln((1 - \alpha)X_2 / aD) - \ln(\alpha X_2 / D). \end{aligned} \quad (8)$$

It is possible to apply this model to any thermodynamic property. For example, the total volume of such a system can readily be expressed in terms of the partial molar volumes of each species:

$$V = n_2 \alpha V_A^0 + n_2(1 - \alpha) V_A^0 + n_1 V_1^0. \quad (9)$$

In this ideal model all the partial molar volumes and the aggregation number a are by definition constants. Equation (9) can now be expressed in any convenient form which corresponds to the measurable data. In the present case, the most convenient quantity is the excess volume defined by:

$$V^E = (V - n_2 V_2^0 - n_1 V_1^0) / (n_1 + n_2) \quad (10)$$

where the standard state for the two components is the pure liquid, i.e., $V_i^0 = V_i^*$. If the fraction of monomers in the pure alcohol ($X_2 = 1$) is denoted by α^* , it then follows that the reduced excess volume is given by:

$$V^E / X_1 X_2 = (\alpha^* - \alpha) (V_A^0 - V_A^0) / X_1. \quad (11)$$

This function is proportional to apparent molar volumes at both ends of the concentration scale. It is therefore a function which remains sensitive to the various types of interactions over the whole mole fraction range. Equations (8) and (11) can readily be solved simultaneously if $\Delta\mu_A$, ΔV_A and a are known. This function was simulated and compared with typical data for alcohol-water mixtures in figure 1. As it stands, this "ideal" model accounts for the increase in volume that is generally observed with these systems but fails to explain the initial decrease in volume in the water-rich end. There are also noticeable differences in the alcohol-rich end. Extra parameters were therefore required to simulate the correct experimental data.

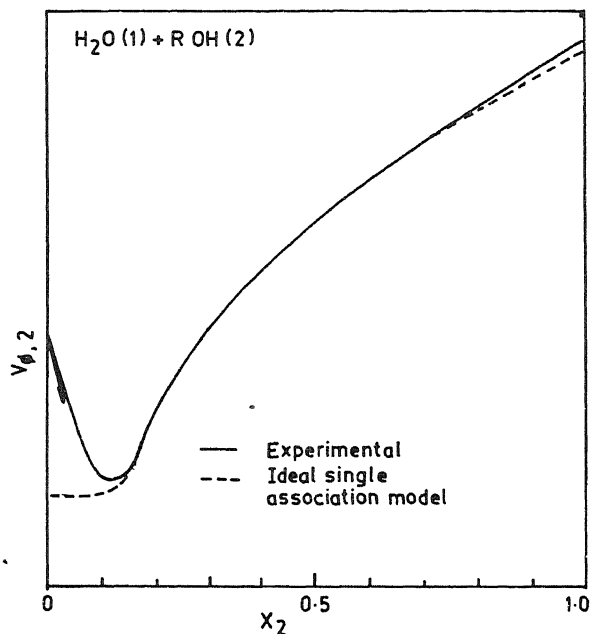


Figure 1. Dependence on the solute mole fraction of the apparent molar volume of alcohols in water, based on the ideal single association model.

4. Single equilibrium non-ideal model

The initial negative slope that is observed with the apparent volumes of hydrophobic solutions in water is generally attributed to the overlap of hydrophobic hydration cospheres when two solutes approach each other (Desnoyers and Jolicoeur 1982). With dilute solutions this effect can be accounted for by the addition of the pair interaction term between monomers (Desnoyers *et al* 1983). With liquid mixtures, this type of non-ideality can be introduced in a form similar to the regular solution theory by introducing two extra terms to (11):

$$V^E/X_1X_2 = (\alpha^* - \alpha)(V_A^0 - V_A^0)/X_1 + B_{v,A}\alpha X_1 + B_{v,A'}(1 - \alpha)X_1, \quad (12)$$

To be consistent, two extra terms of the type $B_{G,A} \alpha X_1$ should also be added to (8). However, with four extra adjustable parameters of this type, the model becomes of questionable use. Therefore, interaction terms were added only to the volume expression as it was done with surfactant systems (Desnoyers *et al* 1983).

Equations (8) and (12) were solved simultaneously and the parameters were optimized using an appropriate non-linear least-squares. For this purpose, the data of Benson and Kiyohara (1980) were used. These simulations are compared with the actual experimental data for the three lower normal alcohols in figures 2 to 4. The parameters derived from these fits are given for different temperatures in table 1 and plotted against temperature in figures 5 and 6.

The general trends for the volumes of the alcohol-water mixtures are accounted for reasonably well with this non-ideal model. However, the deviations between

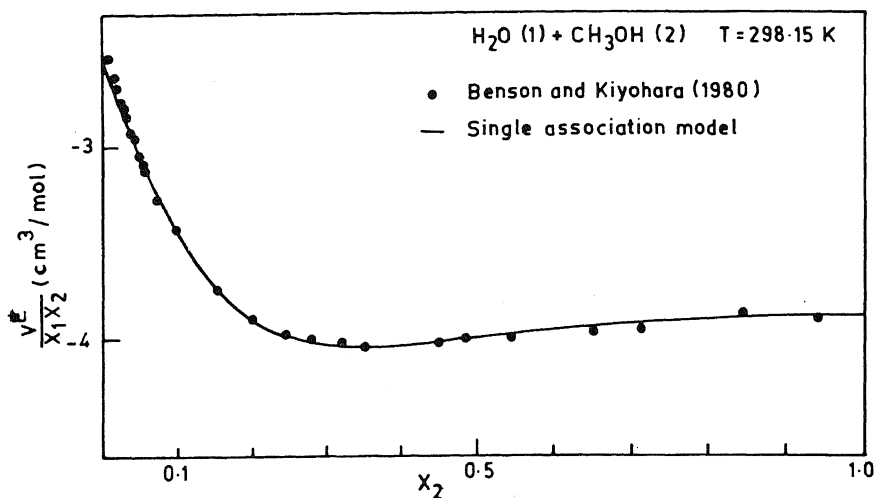


Figure 2. Simulation of the reduced excess volume of methanol-water mixtures with the non-ideal single association model.

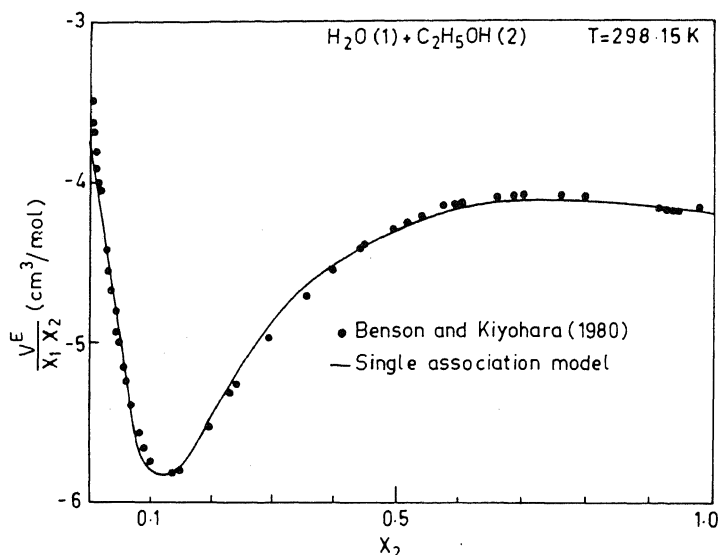


Figure 3. Simulation of the reduced excess volume of ethanol-water mixtures with the non-ideal single association model.

the simulations are the experimental data are definitely larger than the experimental scatter of points. The magnitude of the parameters, especially V_A and a , are not unreasonable. The aggregation number, on the other hand, is assumed to be independent of temperature and pressure in the model, but figure 6 shows that this is not so. With surfactants, the aggregation numbers are also generally found to decrease with temperature as observed here with alcohols. This non-ideal association model can reproduce the experimental reduced excess volumes and at least three of the adjustable parameters have magnitudes that are as expected. On the other hand, the two interaction parameters cannot easily be rationalized. But

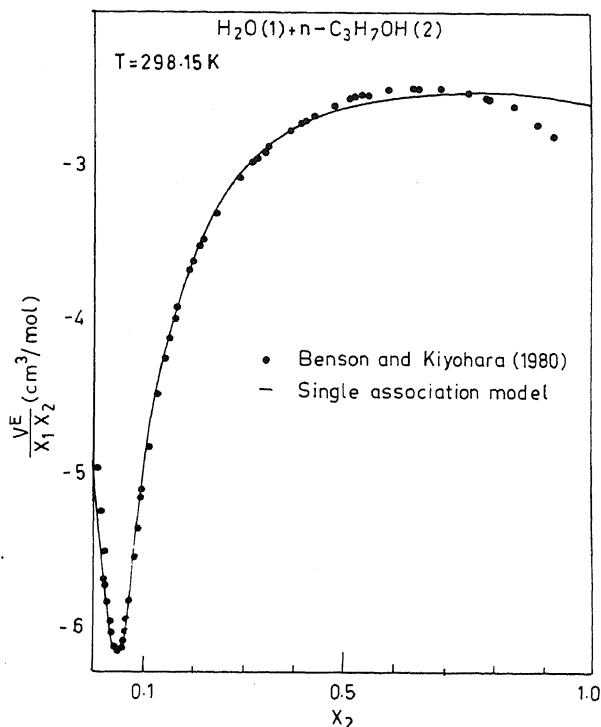


Figure 4. Simulation of the reduced excess volume of *n*-propanol-water mixtures with the non-ideal single association model.

the main failure of this model is that it does not explicitly take into account the high degree of structure of liquid water which should be quite different at both ends of the concentration scale.

5. Double association model

In the non-ideal single association model, all changes in the structure of water are included in the two interaction parameters. A more satisfactory approach would be to take water as an associated liquid, somewhat in the way suggested by Mikhailov (1968) and Hvidt (1978). Again, for simplicity, a two-state model is used for liquid water. To the relations for the alcohol, (1), (3) and (4), similar ones must now be added for water. If the clusters of water *L* are made up of *b* water molecules *B'*,



where *B* represents water in the monomeric form. As with the alcohol, we define the fraction of monomers of water by

$$\beta = n_B/n_1 \quad (14)$$

and the number of clusters by

$$n_L = n_1(1 - \beta)/b. \quad (15)$$

Table 1. Parameters for the "non-ideal single association model".

	$T(^{\circ}\text{C})$	ΔV_A (cm^3/mol)	B_A (cm^3/mol)	B'_A (cm^3/mol)	$\Delta\mu_A$ (J/mol)	a	$\sigma(V^E/x_1x_2)$ (cm^3/mol)	X_2 range
MeOH	15	9.090	5.653	-0.757	1802	4.25	0.022	0.00136
		(0.141)	(0.131)	(0.095)	(26)	(0.09)		0.97751
	20	8.661	4.858	-0.645	1574	4.05	0.014	0.00246
		(0.092)	(0.088)	(0.077)	(20)	(0.05)		0.89691
	25	8.320	4.059	-0.365	1273	3.83	0.012	0.00293
		(0.080)	(0.075)	(0.075)	(18)	(0.04)		0.94059
	30	8.327	3.633	-0.325	1072	3.61	0.009	0.00503
		(0.086)	(0.080)	(0.064)	(20)	(0.04)		0.89421
	35	8.387	3.253	-0.177	874	3.44	0.008	0.00299
		(0.082)	(0.074)	(0.070)	(19)	(0.04)		0.88414
EtOH	15	14.778	10.642	1.507	3118	7.87	0.069	0.02444
		(0.367)	(0.426)	(0.252)	(76)	(0.29)		0.87773
	20	13.600	9.061	1.769	2903	6.72	0.050	0.02395
		(0.332)	(0.387)	(0.158)	(70)	(0.17)		0.93869
	25	13.430	8.680	1.889	2852	6.17	0.048	0.01477
		(0.243)	(0.280)	(0.099)	(50)	(0.11)		0.97325
	30	12.350	7.237	1.809	2650	5.53	0.031	0.02032
		(0.190)	(0.224)	(0.073)	(46)	(0.08)		0.97151
	35	11.888	6.486	1.853	2517	5.06	0.028	0.02034
		(0.198)	(0.236)	(0.083)	(53)	(0.08)		0.96956
nPrOH	15	19.861	14.728	1.757	4653	8.85	0.041	0.02460
		(0.487)	(0.545)	(0.100)	(77)	(0.41)		0.84002
	20	18.884	13.616	1.763	4577	7.60	0.048	0.02046
		(0.519)	(0.577)	(0.096)	(87)	(0.33)		0.88124
	25	17.723	12.310	1.396	4604	6.92	0.031	0.02053
		(0.245)	(0.275)	(0.053)	(48)	(0.16)		0.84634
	30	16.242	10.661	1.499	4428	6.03	0.043	0.02018
		(0.438)	(0.495)	(0.081)	(92)	(0.24)		0.92674
	35	15.659	10.017	1.342	4496	5.74	0.051	0.01363
		(0.558)	(0.623)	(0.095)	(123)	(0.26)		0.96426

Equation 5 becomes:

$$D = X_2[\alpha + (1 - \alpha)/a] + X_1[\beta + (1 - \beta)/b]. \quad (16)$$

The total Gibbs free energy is now given by

$$\begin{aligned} G/RT = & n_2\alpha[\mu_A^0/RT + \ln(\alpha X_2/D)] + \\ & [n_2(1 - \alpha)/a]\{\mu_M^0/RT + \ln[(1 - \alpha)X_2/aD]\} + n_1\beta[\mu_B^0/RT + \ln(\beta X_1/D)] \\ & + [n_1(1 - \beta)/b]\{\mu_L^0 + \ln[(1 - \beta)X_1/bD]\}. \end{aligned} \quad (17)$$

If a and b are independent of the composition, the double stability of the system implies that we have simultaneously:

$$\begin{aligned} & [\partial(G/RT)/\partial\alpha]_{T,P,n_1,n_2,\beta} = 0 \\ & = n_2\{[\mu_A^0/RT + \ln(\alpha X_2/D)] - (1/a)[\mu_M^0/RT + \ln((1 - \alpha)X_2/aD)]\}, \end{aligned} \quad (18a)$$

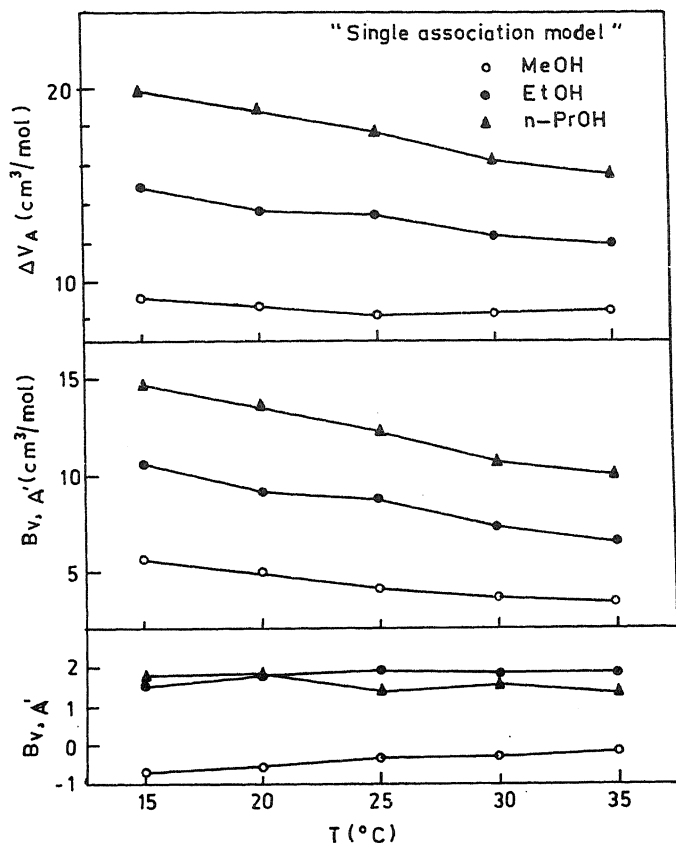


Figure 5. Temperature dependence of the parameters ΔV_A , and $B_{V,A}$ and $B_{V,A}'$ of alcohol-water mixtures extracted from the non-ideal single association model.

and

$$\begin{aligned} & [\partial(G/RT)/\partial\beta]_{T,P,n_1,n_2,\alpha} = 0 \\ & = n_1 \{ [\mu_B^0/RT + \ln(\beta X_1/D)] - (1/b) [\mu_L^0/RT + \ln((1-\beta)X_1/bD)] \}. \end{aligned} \quad (18b)$$

The solution of these two equations will give $\Delta\mu_A$ and $\Delta\mu_B$ in terms of α , β , a and b .

The total volume of the system is given by

$$V = n_2\alpha V_A^0 + n_2(1-\alpha)V_A^0 + n_1\beta V_B^0 + n_1(1-\beta)V_B^0, \quad (19)$$

If, as in the case of the single equilibrium model, the fraction of monomers in the pure water ($X_1 = 1$) to given by β^* , then the reduced excess volume is given by

$$V^E/X_1X_2 = (\alpha^* - \alpha)\Delta V_A/X_1 + (\beta^* - \beta)\Delta V_B/X_2. \quad (20)$$

The excess volume is now a function of six parameters all of which have a physical significance: $\Delta\mu_A$, $\Delta\mu_B$, a , b , ΔV_A and ΔV_B . These experimental points from other authors are also included in these figures to give some idea of the scatter of the data when plotted in this fashion but were not used in the least-squares. The derived parameters for various temperatures are summarized in table 2.

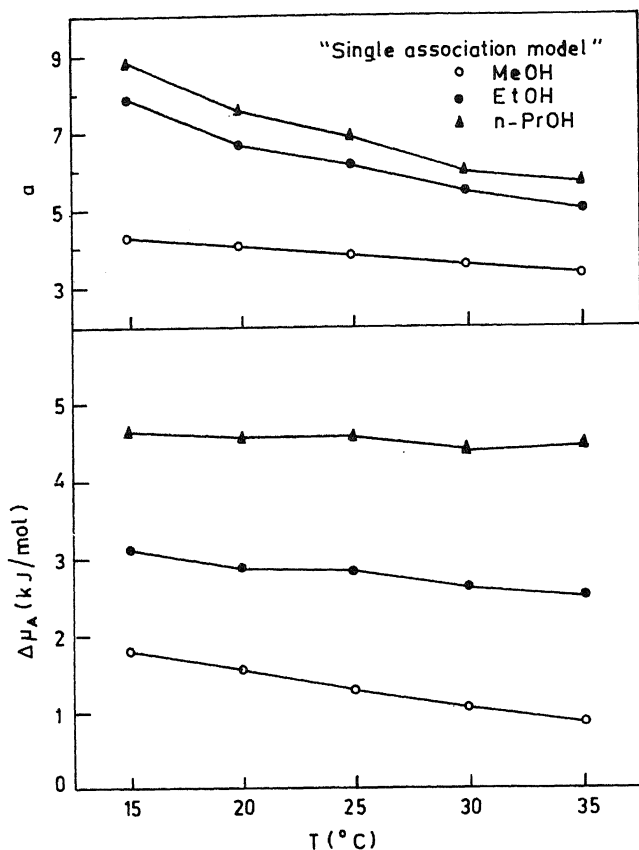


Figure 6. Temperature dependence of the parameters $\Delta\mu_A$ and a of alcohol-water mixtures extracted from the non-ideal single association model.

The fit between the simulations and experimental data is excellent in all cases for intermediate mole fractions. Therefore, only the water-rich and alcohol-rich regions are shown in figures 7 to 9. The fit is essentially quantitative over the whole mole fraction range in the case of MeOH and EtOH. The agreement is also excellent in the water-rich region with *n*-PrOH but less good in the alcohol-rich region. This kind of plot and simulation illustrates very well the necessity of obtaining precise data over the whole mole fraction region, especially to very low and very high mole fraction. For example, we were unable to simulate enthalpy data from the literature since the dilute region and concentrated one were not measured by the same authors and the disagreement between the different sets of data were too large.

The various parameters obtained from the model are plotted against temperature in figures 10 to 13. The trends of V_A (figure 10) are not unexpected but their magnitudes, especially with the higher homologs, seem high. The aggregation numbers a of the alcohols (figure 12) do not change in a regular way, their magnitude seem high, especially with *n*-PrOH, and vary with temperature while the model assumes a to be independent of temperature. The trends and magnitudes of $\Delta\mu_B$, ΔV_B and b should also have been independent of the alcohol if the role of

Table 2. Parameters for the "ideal double association model".

	$T(^{\circ}\text{C})$	ΔV_A (cm^3/mol)	$-\Delta V_B$ (cm^3/mol)	$\Delta \mu_A$ (J/mol)	$\Delta \mu_B$ (J/mol)	a	b	$\sigma(V^E/x_1x_2)$ (cm^3/mol)	X_2 range
MeOH	15	8.893	2.309	1533	185	7.08	14.49	0.010	0.02536 0.86127
	20	8.332	2.160	1422	172	6.79	12.81	0.009	0.02463 0.89691
	25	8.328 (0.018)	2.187 (0.027)	809 (15)	-543 (22)	4.07 (0.05)	7.85 (0.08)	0.007	0.00809 0.94059
	30	7.948	1.912	869	-331	4.48	7.99	0.006	0.02451 0.89421
	35	7.841	1.898	695	-458	4.24	6.96	0.002	0.02882 0.88414
EtOH	15	19.124	6.482	2109	-156	6.17	10.32	0.010	0.02444 0.94196
	20	18.059	5.904	2095	-115	6.13	10.28	0.012	0.01921 0.94698
	25	17.882 (0.013)	6.697 (0.032)	1952 (3)	-391 (6)	4.93 (0.02)	8.22 (0.04)	0.012	0.00089 0.93984
	30	16.002	5.179	1974	-126	5.61	9.37	0.010	0.02032 0.94760
	35	15.694	5.416	1847	-278	4.89	8.07	0.007	0.02034 0.93263
nPrOH	15	45.512	12.241	3210	514	26.01	73.8	0.052	0.00274 0.97225
	20	32.522	7.361	3392	416	18.12	55.73	0.031	0.00830 0.79079
	25	27.402 (1.675)	5.853 (0.510)	3356 (33)	333 (47)	11.6 (1.7)	37.6 (5.6)	0.047	0.02053 0.92388
	30	22.571	4.829	3282	331	10.1	31.8	0.046	0.01442 0.92674
	35	19.434	3.497	3514	231	8.84	29.7	0.027	0.00800 0.79013

the alcohol was simply to perturb the monomer-cluster equilibrium of water. Figures 11 and 13 show that this is certainly not so. We can therefore conclude from these simulations that, although the prediction of the observed trends are, in general, excellent with this double equilibrium model, the parameters extracted and their trends with temperature are not always realistic.

6. Discussion

A mass-action model (Desnoyers *et al* 1983) has been used successfully to fit the thermodynamic properties of non-ionic surfactants in water and extract from these the functions of micellization. The equilibrium constants and aggregation numbers were of the right order of magnitude and, as a first approximation, independent of the property. This model has presently been generalized to include all systems that

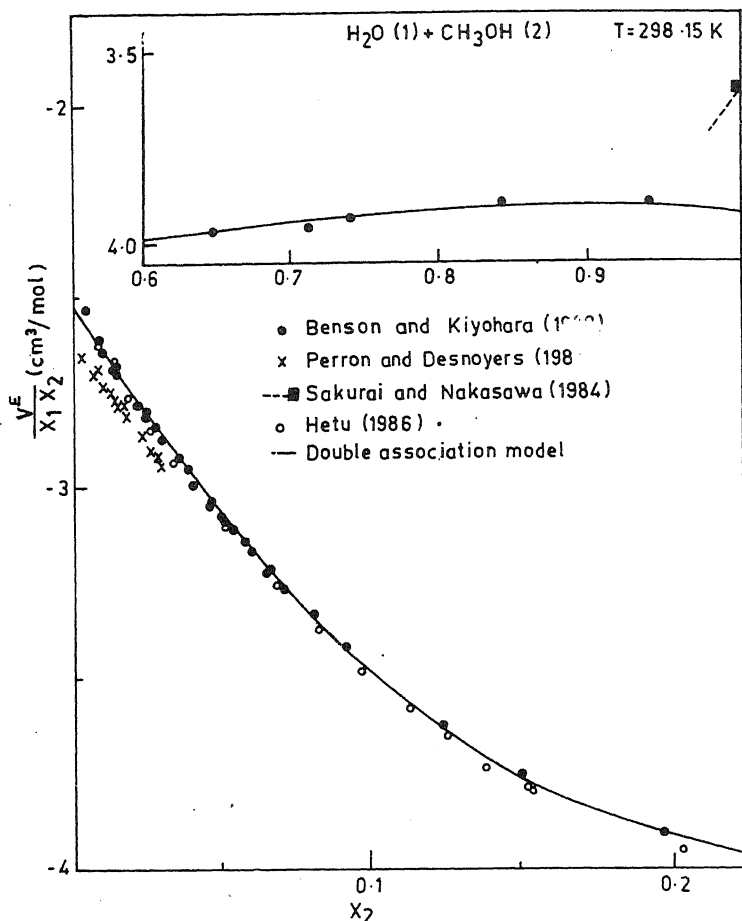


Figure 7. Simulation of the reduced excess volume of methanol-water mixtures with the double association model.

form microaggregation in water. Two variances of this micellar model have been applied to volume data of alcohol-water mixtures.

The main advantage of the present approach is that the models apply equally well to systems which show concentration microheterogeneity and to the micellar systems. The models can also readily be extended to all thermodynamic properties. The non-ideal single equilibrium model fits reasonably well the reduced excess volumes, and the three basic parameters, $\Delta\mu_A$, ΔV_A and a , are of the right order of magnitude and vary as expected with chain length of the alcohol. On the other hand, a varies with temperature, contrary to the basic assumption of the model, and the parameters $B_{V,A}$ and $B_{V,A'}$ have no simple molecular meaning. The double equilibrium model fits the data better, and all the parameters have a physical meaning. However, the magnitude and trends of these parameters are not always as expected. In particular, the parameters for water depend on the alcohol, which is contrary to the basic assumption that the role of the alcohol was simply to shift the monomer-cluster equilibrium of water.

As mentioned in §2, a severe test of these models would be to apply them to

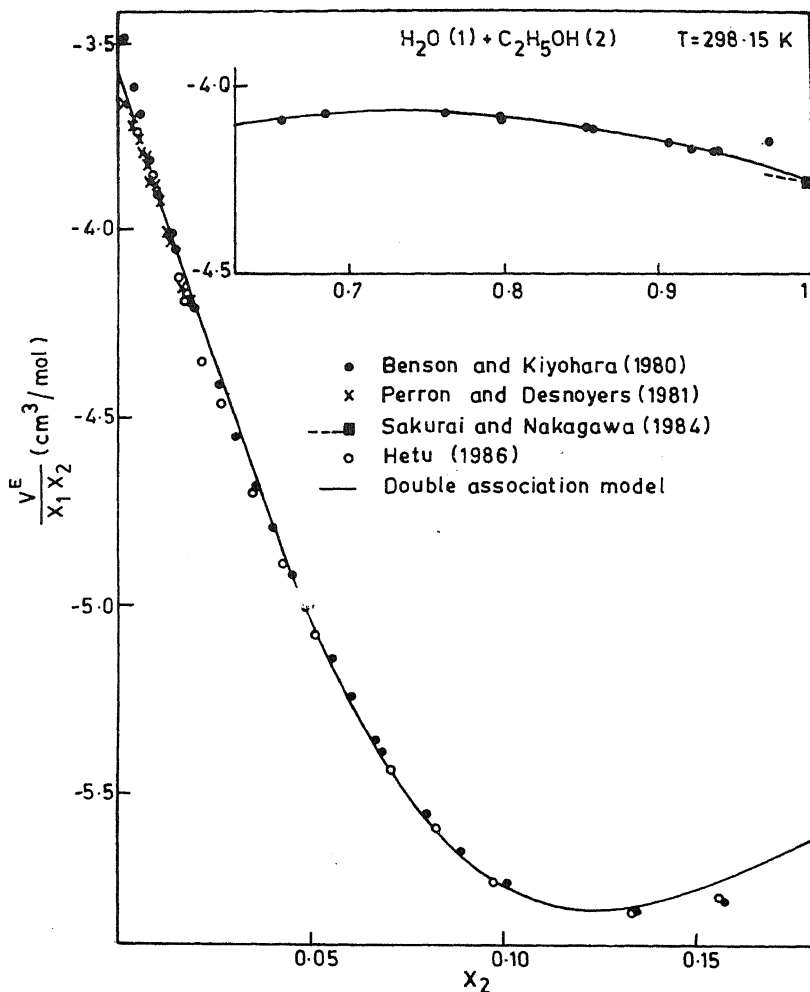


Figure 8. Simulation of the reduced excess volume of ethanol-water mixtures with the double association model.

different properties and check to see if $\Delta\mu_A$, a and the parameters for water remain independent of the properties. Unfortunately, free energies and enthalpies have not been measured with sufficient precision over the whole mole fraction range, including the very dilute regions, to treat the data the way we did with volumes. Reasonably good data exist for heat capacities and compressibilities, but these functions, being second derivatives of the chemical potential with respect to temperature or pressure, must automatically include terms for the displacement of the equilibrium with temperature or pressure, and this will add extra adjustable parameters.

Many of the oversimplified assumptions of these models could be responsible for their weaknesses. The three main ones are:

1. The aggregation numbers are not constants with respect to temperature and pressure.

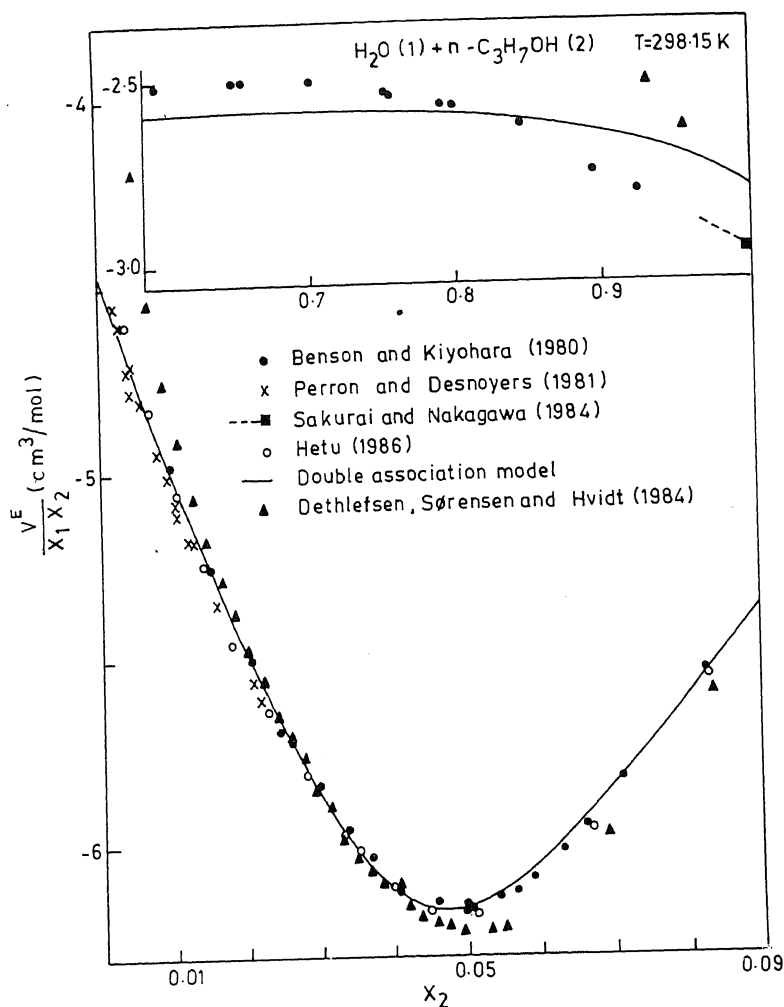


Figure 9. Simulation of the reduced excess volume of *n*-propanol-water mixtures with the double association model.

2. The size of the alcohol aggregates and of water clusters are not independent of alcohol and of water concentration.
3. The aggregates and clusters are not monodispersed.
4. The structure of water in the hydrophobic copheres certainly has some differences with the clusters which exist in pure water.

The models can readily be correlated for all these effects but at the expense of extra parameters. Also, in such cases, the convergence of the least-squares will be much slower.

The double equilibrium model is therefore a good curve-fitting model since it uses the minimum number of adjustable parameters necessary to fit the observed thermodynamic data, but, as it stands, it does not provide much insight on the structure of these systems. It does suggest however promising paths for the

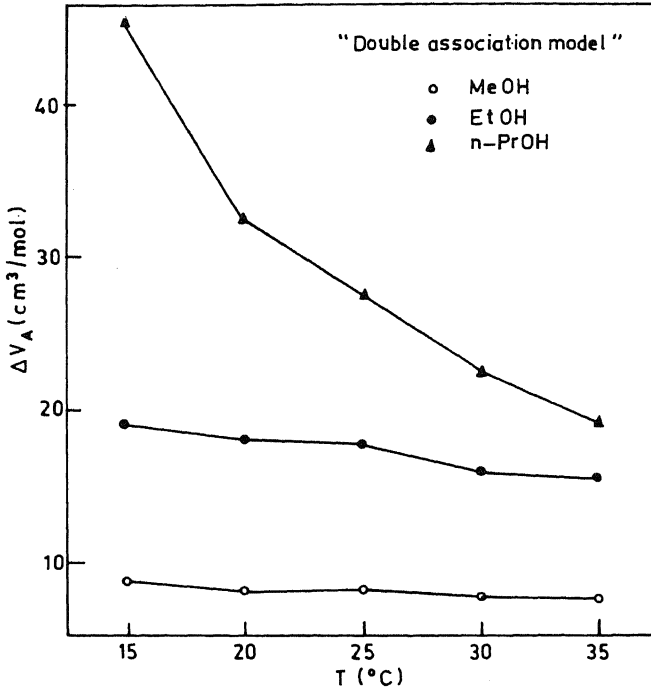


Figure 10. Temperature dependence of the parameter ΔV_A of alcohol-water mixtures extracted from the double association model.

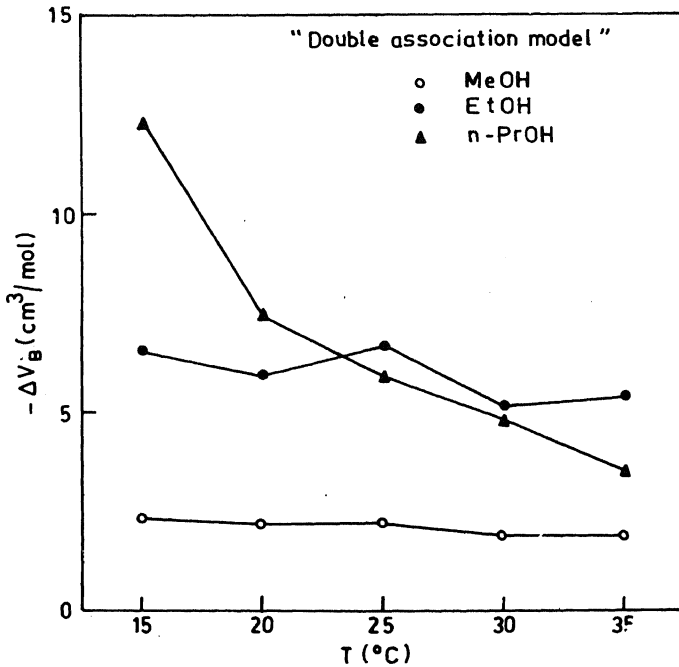


Figure 11. Temperature dependence of the parameters ΔV_B of alcohol-water mixtures extracted from the double association model.

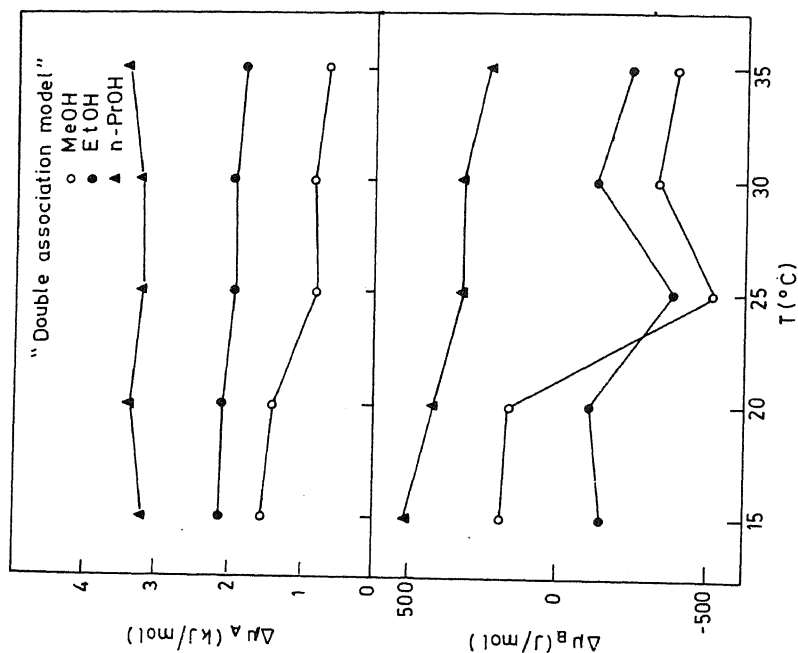


Figure 12. Temperature dependence of the parameters $\Delta\mu_A$ and $\Delta\mu_B$ of alcohol-water mixtures extracted from the double association model.

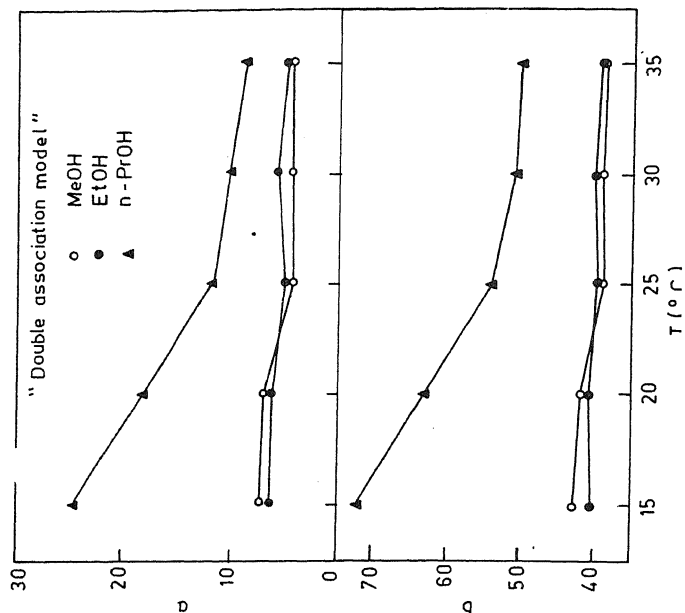


Figure 13. Temperature dependence of the parameters a and b of alcohol-water mixtures extracted from the double association model.

development of successful models for these systems. For example, the mass-action model for the micellar system can be introduced, as it was done here, with a more appropriate theory for liquid water, where all the water parameters would be fixed by the pure liquid.

Acknowledgements

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Solubilization of bilirubin by cholate micelles. Spectroscopic and gel permeation studies

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Abstract. The interactions of bilirubin with bile salts have been studied using fluorescence, circular dichroism and ^1H NMR methods. Enhancement of bilirubin fluorescence and induction of optical activity in bilirubin in the presence of cholate has been observed. Fluorescence enhancement is pronounced above the critical micelle concentration, while induced CD bands are detectable even in the premicellar region. Dehydrocholate and deoxycholate did not cause a fluorescence increase, but induced CD bands were observed for bilirubin in these cases. Gel permeation chromatography on Sephadex G-50 yielded a single bilirubin-cholate species at alkaline pH, while two species were obtained at neutral pH. ^1H NMR and CD spectral characterizations of these complexes are reported. A 4:1 cholate-bilirubin mixture has been analysed by difference (nuclear Overhauser effect) NOE spectroscopy. Observation of strong, negative NOE, both intermolecular and intramolecular leads to the conclusion that specific methyl groups on bilirubin and cholate are proximal in the mixed micelle.

Keywords. Bilirubin; bile salts; micelles; induced circular dichroism; fluorescence; nuclear Overhauser effects.

1. Introduction

An important aspect of biliary physical chemistry is the physical state of organic anions in bile. Bilirubin is one of the most thoroughly studied anions because of its biological and clinical importance. Other anions are drugs and dyes like indocyanine green, bromsulphthalein, rose bengal etc. Many of these are incorporated into mixed micelles of lipids and bile acids (Bickel and Minder 1970; Scharshmidt and Schmid 1978; Reuben *et al* 1982). A physical association with lipid micelles helps in the effective excretion of the xenobiotics in bile (Reuben 1984).

Bilirubin IX α is the end product of heme degradation in mammals (Brown and Troxler 1982) which has necessarily to be excreted as it serves no useful purpose and is neurotoxic. Bilirubin is practically insoluble under physiological conditions and is transported in blood as the serum albumin complex (Meuwissen and Heirwegh 1982) to the liver, where it undergoes conjugation with glucuronic acid to form the more soluble diglucuronides. In the case of bilirubin, the rate of biliary secretion has been shown to rise with an increase in biliary output of bile salts (Goresky *et al* 1974). The solubility of bilirubin has been found to be enhanced in the presence of bile salts (Carey and Koretsky 1979; Ostrow and Celic 1984). Bilirubin is therefore thought to be associated with mixed micelles of lecithin and bile salts. However, structural details of such an interaction between bilirubin and

bile salts are lacking and that has prompted us to undertake a spectroscopic investigation of this system. This report summarizes fluorescence, circular dichroism (CD), gel permeation and ^1H NMR studies of bilirubin-bile salt complexes.

2. Materials and methods

Bilirubin obtained from Sigma Chemical Co. was purified according to the procedure of McDonagh and Assisi (1972). Cholic acid, dehydrocholic acid and sodium deoxycholate were also from Sigma. Both cholic acid and dehydrocholic acid were converted into their sodium salts by adding a molar equivalent of sodium hydroxide and subsequent lyophilization.

Aqueous stock solutions of bilirubin were prepared using sodium hydroxide for complete dissolution. The concentration of such stock solutions was determined using $\epsilon_{438} = 47,000 \text{ M}^{-1}\text{cm}^{-1}$ (Carey and Koretsky 1979). The solutions were used within two to three hours of preparation. Samples containing bilirubin and cholate for ^1H NMR studies were made by addition of solid bilirubin to the cholate solution in D_2O and then increasing the pD of the solution to ~ 10.5 using NaOD, when all the bilirubin dissolves. Such samples could be stored in the dark, at 4°C , for at least two days without the occurrence of bilirubin photodegradation.

For the fluorescence and CD experiments the final concentration of bilirubin used was always less than $1 \times 10^{-5} \text{ M}$. 1 cm pathlength cuvettes were used for the fluorescence experiments, while for the CD experiments a 5 cm pathlength, cylindrical cell was employed. Fluorescence studies were carried out on Perkin Elmer MPF 44A and Hitachi 650-60 fluorimeters and CD studies on a JASCO J20 spectropolarimeter.

Gel permeation studies were done on a Sephadex G-50 column of dimensions $1.1 \text{ cm} \times 70 \text{ cm}$. Blue dextran (Sigma) was used to check the column packing as well as to determine the void volume. The column was calibrated using proteins like melittin (monomeric), cytochrome c from horse heart and ovalbumin. The sample volume loaded varied between 150 and $300 \mu\text{l}$. In the case where ^1H NMR spectra of column fractions are reported, the appropriate fractions were pooled, lyophilized and redissolved in D_2O .

^1H NMR spectra were recorded on a Bruker WH-270 FT NMR spectrometer at the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore. No external standard was added to the sample, the 4.76 ppm resonance of H_2O (in D_2O) was taken as an internal reference. All experiments were done at 293 K. Difference nuclear Overhauser effect (NOE) spectra were obtained by sequential recording of perturbed and normal spectra (8 K memory each) using low power on-resonance shifting of the irradiation frequency, respectively. A delay time of 3.0 sec was used between transients. The difference free induction decay was multiplied by a decaying exponential, prior to Fourier transformation.

3. Results

The linear structure of bilirubin IX α , the physiologically important bilirubin isomer, is shown in figure 1. Also shown in figure 1 is the structure of cholate, the

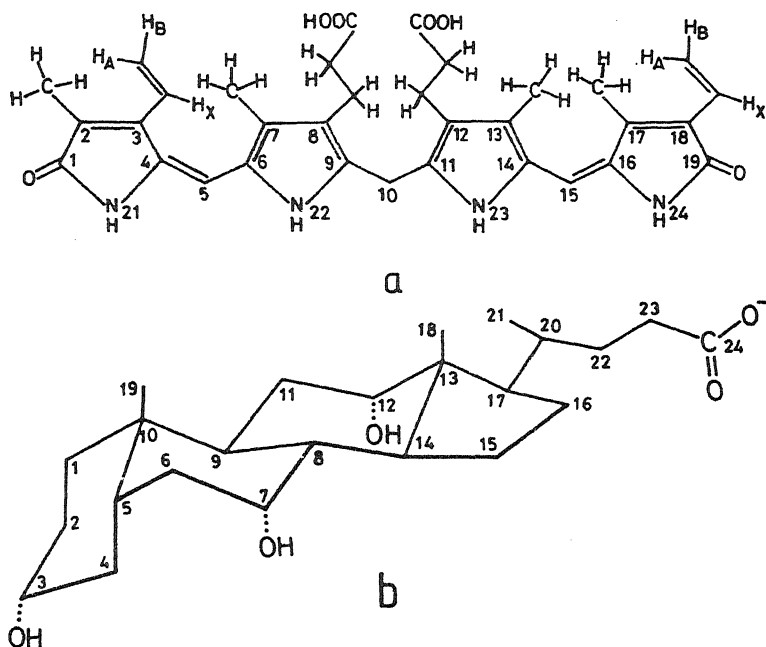


Figure 1. (a) Structure of bilirubin IX α (4Z, 15Z configuration) with numbering scheme. (b) Structure of cholate with numbering scheme.

bile salt which is the subject of most of the studies described in this report. The other bile salts studied are deoxycholate which lacks a hydroxyl group at position 7 and dehydrocholate, where all the three hydroxyl groups are replaced by keto groups.

3.1 Fluorescence

Figure 2 shows the enhancement of bilirubin fluorescence in the presence of sodium cholate. Bilirubin is practically non-fluorescent in solution at room temperature, the quantum yield being less than 10^{-4} (Matheson *et al* 1975). Binding to serum albumin results in fluorescence enhancement. This increase has been attributed to translational and vibrational immobilization of bilirubin in its bound form (Beaven *et al* 1973). Bilirubin has also been shown to exhibit enhanced fluorescence when it binds to gramicidin S (Marx-Leisy *et al* 1985) and symmetrical alkyl diamines (Lahiri and Balaram 1987). Increase of bilirubin fluorescence in the presence of other macromolecules can thus be considered as indicating interaction leading to binding. It is interesting to note in figure 3 that the enhancement of bilirubin fluorescence in the presence of varying concentrations of cholate exhibits a sharp discontinuity around 13 mM, followed by a further rise. The critical micelle concentration (CMC) of cholate is known to be between 11 and 13 mM (Roda *et al* 1983), depending on the presence of salts like sodium chloride. It thus appears that bilirubin binds preferentially to micelles of cholate. There is no observed increase in the fluorescence of bilirubin in the presence of the other bile salts, deoxycholate and dehydrocholate. While the CMC of deoxycholate is ~ 10 mM, that of dehydrocholate is > 250 mM (Roda *et al* 1983).

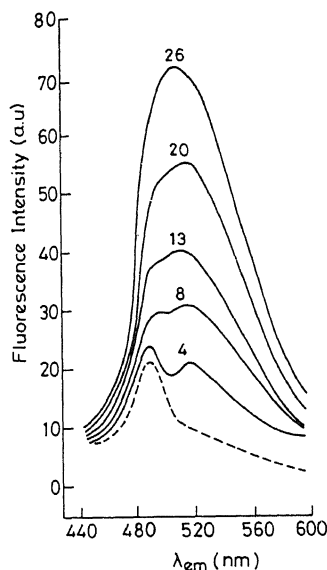


Figure 2. Enhancement of bilirubin (4.8×10^{-6} M) fluorescence (arbitrary units) in the presence of cholates in H_2O at pH 10.9, 150 mM NaCl. Number over each trace indicates the cholates concentration in mM $\lambda_{\text{ex}} = 420$ nm.

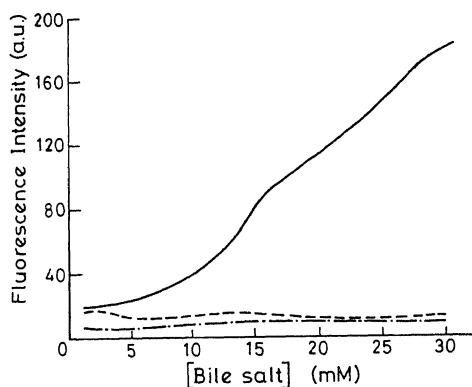


Figure 3. Dependence of bilirubin fluorescence on the concentration of bile salts in H_2O , pH 10.8, 150 mM NaCl. $\lambda_{\text{ex}} = 420$ nm, $\lambda_{\text{em}} = 520$ nm. (— 4.6×10^{-6} M bilirubin in cholates; --- 7.3×10^{-6} M bilirubin in deoxycholate; -.- 7.3×10^{-6} M bilirubin in dehydrocholate.)

3.2 Circular dichroism

CD is a useful technique to monitor bilirubin binding to other molecules since the observation of induced optical activity in the otherwise optically inactive bilirubin is a positive indication of the occurrence of such interactions (Blauer 1983). Such induced optical activity is observed when bilirubin binds to proteins like serum albumins (Brodersen 1982), ligandin (Bhargava *et al* 1980), aminoazodye-binding protein A (Tipping *et al* 1976) and chymotrypsin and lysozyme (Blauer 1986). Bilirubin also exhibits induced CD when bound to chiral amines and basic

polypeptides like poly-L-lysine, melittin and gramicidin S (Marr-Leisy *et al* 1985). Induced optical activity has been observed for bilirubin in the presence of sodium deoxycholate (Perrin and Wilsey 1971). Figure 4 shows the induced CD in 7.6×10^{-6} M bilirubin in the presence of 2×10^{-2} M cholate, deoxycholate and dehydrocholate at pH 10.5. The characteristic bisignate CD pattern is observed with long wavelength positive and short wavelength negative bands, reminiscent of the bilirubin-human serum albumin 1:1 spectrum at $\sim$ pH 7 (Blauer and Harmatz 1972). In the case of bile salts, the long wavelength bands lie between 450 and 470 nm and the short wavelength band between 375 and 400 nm. The CD parameters for bilirubin in the presence of various bile salts are summarized in table 1. The parameters for bilirubin-human serum albumin are also given for comparison. Figure 5 shows the induced CD spectra for bilirubin in presence of increasing concentrations of cholate. The cholate concentrations studied range from 1 to 20 mM. Figure 6 shows a plot of the CD band intensities at 400 and 455 nm as a function of cholate concentration. The results suggest that induced optical activity is detectable even at premicellar cholate concentrations.

3.3 Gel permeation chromatography

To characterize the size of the complex formed by bilirubin and cholate, gel permeation chromatography was performed on a Sephadex G-50 column. A 4:1 cholate-bilirubin mixture in water at pH 10.5 was loaded on the column, the eluant

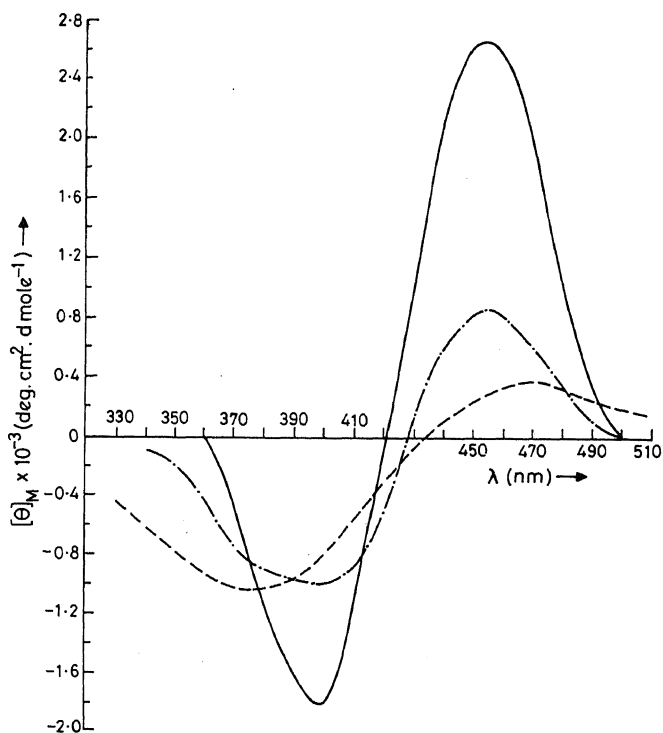


Figure 4. Induced CD spectra of bilirubin (7.6×10^{-6} M) in the presence of 20 mM bile salts in H_2O , pH $\sim$ 10.5, 150 mM NaCl. Cholate (—), deoxycholate (---), dehydrocholate (— · —).

Table 1. CD spectral parameters of bilirubin in presence of bile salts.

Bile salt (serum albumin) ^a	Solvent	Bile salt (HSA) concentration (M)	Bilirubin concentration (M)	λ_{nm} ($[\theta]_M$) ^b
Cholate	H ₂ O, pH 10.6	2×10^{-2}	7.63×10^{-6}	400(-1.0×10^3); 455(0.86×10^3)
Deoxycholate	H ₂ O, pH 10.5	2×10^{-2}	7.68×10^{-6}	375(-1.04×10^3); 472(0.38×10^3)
Dehydrocholate	H ₂ O, pH 10.5	2×10^{-2}	7.68×10^{-6}	398(-1.82×10^3); 453(2.66×10^3)
HSA	H ₂ O, pH 8.7	3.46×10^{-5}	3.46×10^{-5}	397(-1.45×10^5); 448(1.97×10^5)

^a Data taken from Marr-Leisy *et al* 1985; ^b $[\theta]_M$ values as deg. cm². d mole⁻¹.

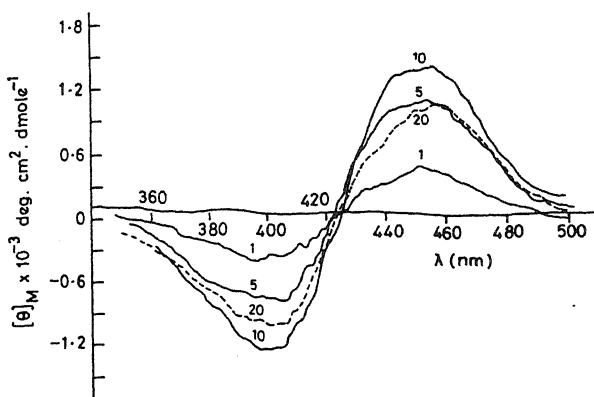


Figure 5. Induced CD spectrum of 6.9×10^{-6} M bilirubin with increasing cholate concentrations in H₂O at pH 9.2 150 mM NaCl. Number over each trace is the concentration of cholate in mM.

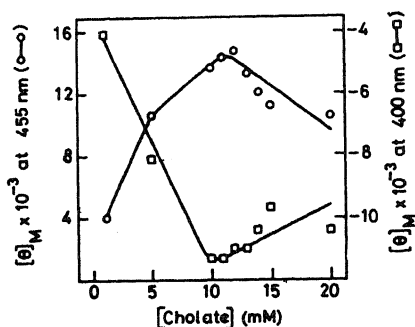


Figure 6. Change in molar ellipticity ($[\theta]_M$) of the bilirubin CD bands at 400 and 455 nm as a function of cholate concentration. ($[\theta]_M$ values as deg. cm². dmole⁻¹).

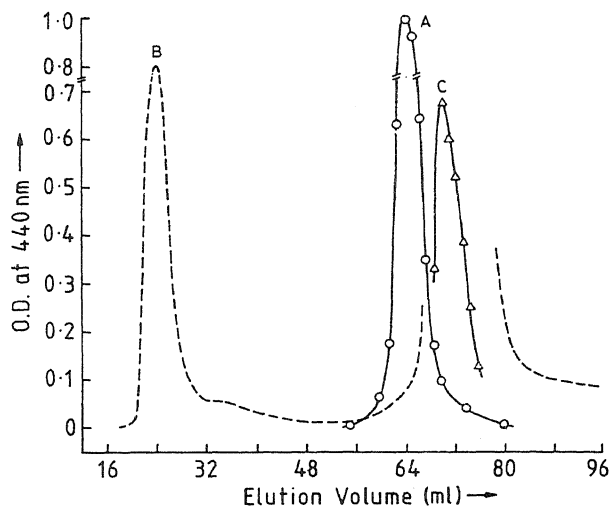


Figure 7. Elution profiles of 15 mM bilirubin in 60 mM cholate, pH 10.5 through a Sephadex G-50 column. Peak A is obtained when the eluant is H_2O at pH 10.8. Peaks B and C constitute the two fractions when eluant is at pH 6.6. (Absorbances of peaks A and C are of diluted samples.)

being water at pH 10.8 or at pH 6.6. The elution profile was found to depend on the the same pH, i.e. alkaline, the elution profile, which is obtained by measuring the absorbance of each fraction at 440 nm, shows a single peak (peak A). On the other hand, when the eluant is at a pH lower than that of the sample loaded, two well-separated peaks (designated as peaks B and C in figure 7) are observed. Peak B which is almost at the void volume of the column must be a relatively high molecular weight fraction (Sephadex G-50 has an exclusion molecular weight of $\sim 30,000$). A cholate solution of similar concentration (60 mM) was also run on the same column under identical conditions. The elution profile of cholate, shown in figure 8, does not depend on the pH of the eluant and coincides with the position of peak A. To estimate the molecular weights of the column fractions, the column was calibrated using standard proteins and a calibration curve obtained (figure 8 inset). From this curve, the molecular weights of the peaks A and C work out to be ~ 1780 and ~ 1120 , respectively.

These column fractions were subjected to CD studies and analysed for their composition using ^1H NMR. For the CD spectra, small aliquots were taken from the desired fraction, diluted in water and its pH adjusted before recording the spectrum. The CD data are summarized in figure 9. It is observed that for peak A, there is no optical activity at a pH of 11.4. At pH 6.7, weak bands appear, which are stronger at pH 2.7. On the other hand, for peak B, CD spectra are observed at both neutral, as well as alkaline pH. Peak C exhibits a CD spectrum at neutral pH but not at alkaline pH. As compared to the CD spectrum of peak B, that of peak C is less intense and has its long wavelength band red-shifted, while its short wavelength band is blue-shifted.

The ^1H NMR spectrum of peak A was found to be identical to that of the bilirubin:cholate 1:4 sample, i.e., the sample which is loaded on the column.

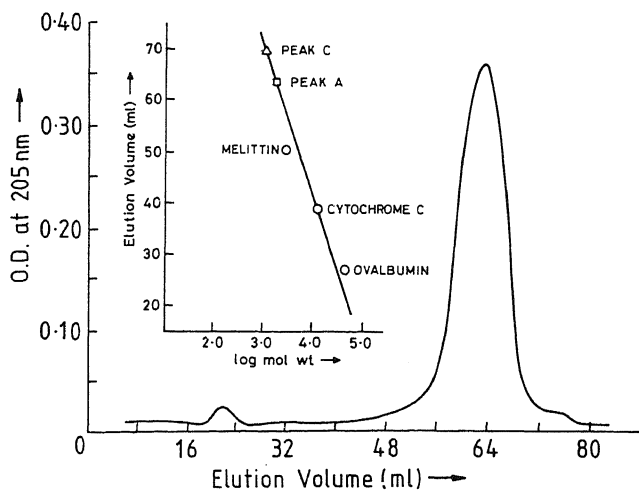


Figure 8. Elution profile of 60 mM cholate through the Sephadex G-50 column. Inset shows the calibration curve, for estimation of molecular weights, of the column using standard proteins. Marked on this are the peak positions of peaks A and C.

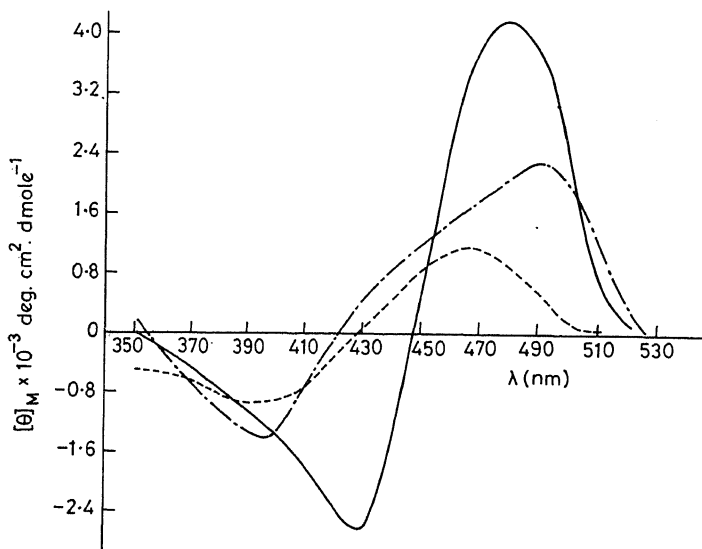


Figure 9. CD spectra of the column fractions. (---) peak A, pH 2.7, 7.45×10^{-6} M bilirubin; (—) peak B, pH 6.7, 5.76×10^{-6} M bilirubin; (-.-.-) peak C, pH 6.7, 4.4×10^{-6} M bilirubin.

Figure 10 shows this spectrum along with some of the main assignments. The assignment of the cholate peaks between 0.7 and 4.0 ppm is taken from Waterhous *et al* (1985), while that of bilirubin in the region 5 and 7 ppm was obtained from decoupling experiments. Integration of the bilirubin and cholate resonances permits an estimate of the stoichiometry of the bilirubin-cholate complex.

Figure 11 shows the ^1H NMR spectrum of peak C. Integration of the bilirubin and cholate resonances establishes that the ratio of bilirubin to cholate is 2:1, which

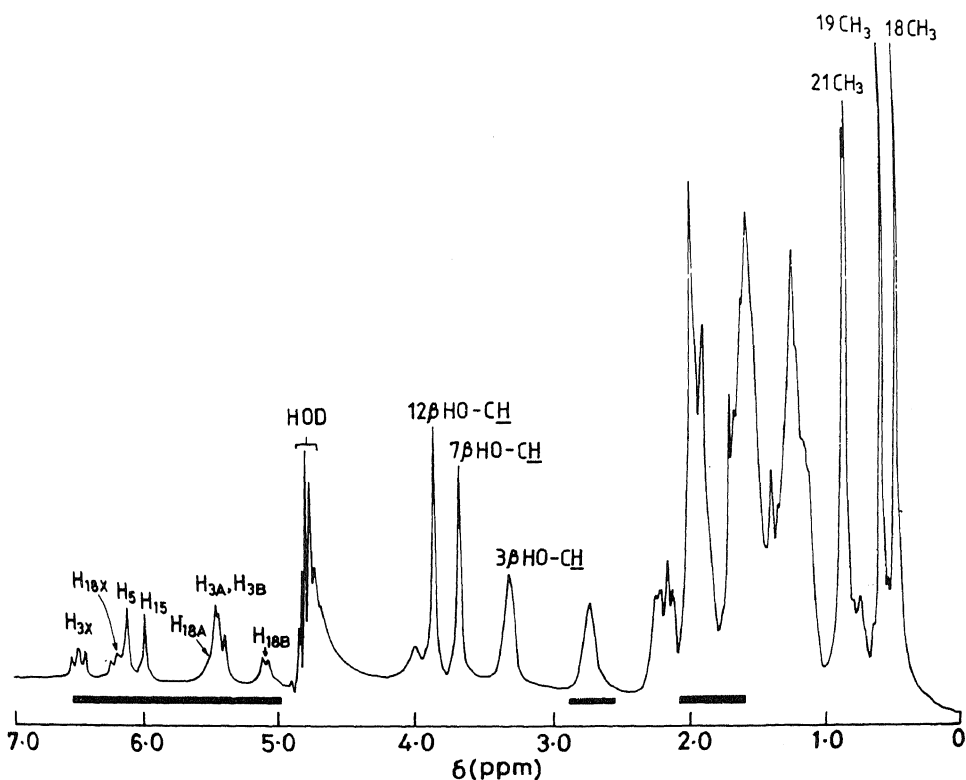


Figure 10. 270 MHz ^1H NMR spectrum of 4:1 cholate-bilirubin (120 mM cholate, 30 mM bilirubin) in D_2O at pH 10.5. Major assignments are shown; the shaded zone indicates the region of bilirubin chemical shifts.

is distinctly different from the composition of the mixture loaded on the column, viz., 1:4 bilirubin:cholate. This is not surprising in itself since peak B obviously corresponds to a large complex with a high cholate to bilirubin ratio, suggesting disproportionation of the original 1:4 bilirubin:cholate mixture.

3.4 Nuclear Overhauser effects

The precise nature of intermolecular interactions can, in principle, be probed by the use of nuclear Overhauser effects (Bothner-By 1979). Spatial proximity of protons (hydrogen atoms) can generally be established for interproton distances of $< 3 \text{ \AA}$. In the case of macromolecular and micellar systems the sign of the observed NOE are dependent on the product of the Larmor precession frequency (ω) and rotational correlation time (τ_c), with positive NOE observed for $\omega\tau_c < 1$, while negative NOE are observed for $\omega\tau_c > 1$ (Bothner-By 1979). Thus, NOE also provide a means of estimating τ_c values which in turn can be related to the molecular size.

One-dimensional NOE measurements were performed on the 1:4 bilirubin:cholate system. Figure 10 shows the 270 MHz ^1H NMR spectrum of a 1:4 mixture of bilirubin and cholate. The olefinic proton resonances of bilirubin are confined to

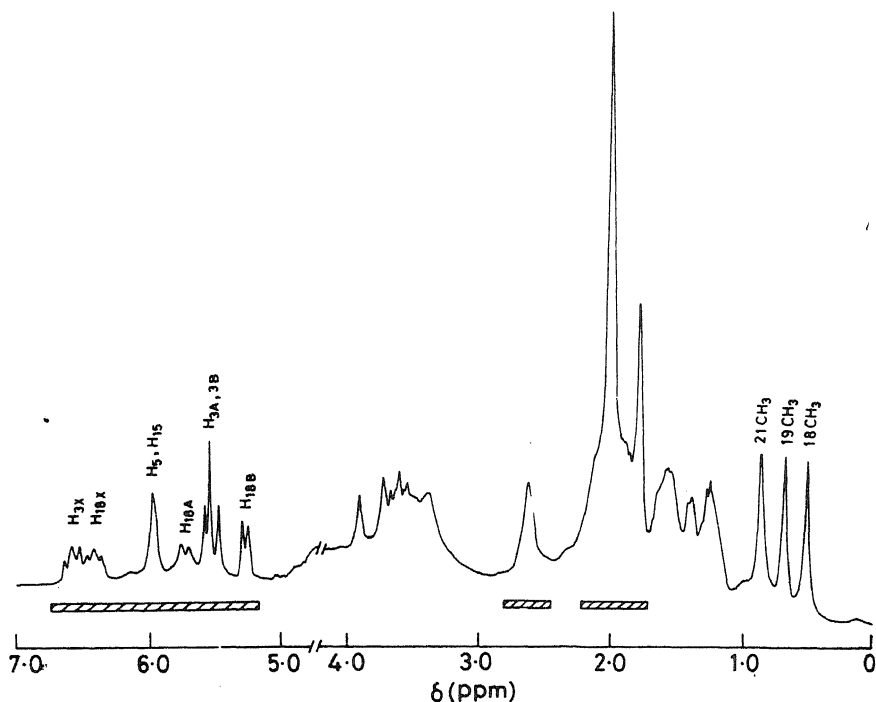


Figure 11. 270 MHz ^1H NMR spectrum of peak C in D_2O , pH 11.5. Specific assignments are indicated. The hatched region corresponds to bilirubin resonances.

the low field region between 5 and 6.7 ppm. The methyl resonance corresponding to the $-\text{CH}_3$ groups at positions 2, 7, 13 and 17 lie between 1.7 and 2.1 ppm. The propionate $-\text{CH}_2$ protons appear at 2.74 ppm. These resonances are marked by a hatched line in figure 10. All the steroid proton resonances of cholate are limited to the spectral region between 0.5 and 4 ppm.

Figure 12 shows the results of representative NOE experiments on the 1:4 bilirubin-cholate mixture. Besides the expected intramolecular NOE, some intermolecular, bilirubin to cholate, NOE are also observed. For example, in figure 12b irradiation of the bilirubin olefinic methyl resonances clearly shows the expected intramolecular NOE on the H_5 and H_{15} methine protons. The proximity of these protons is not clearly evident from the linear structure shown in figure 1a. However, it should be noted that rotation about the C_5-C_6 and $\text{C}_{14}-\text{C}_{15}$ single bonds brings these atoms into close proximity. NOE are also observed on the H_{12} , H_7 and H_3 protons of the steroid. These NOE can be rationalized as intramolecular cholate NOE, since the $\text{H}_{2\beta}$, $\text{H}_{11\alpha}$, $\text{H}_{11\beta}$ and $\text{H}_{6\beta}$ protons have been assigned to resonances in this region (Waterhous *et al* 1985). The spectrum in figure 12c illustrates the effect of irradiating the C_{19} methyl group of cholate. Two strong NOE are observed on the cholate protons $\text{H}_{12\beta}$ and $\text{H}_{7\beta}$. While the NOE on $\text{H}_{12\beta}$ can be rationalized as an intramolecular effect due to partial saturation of the proximate C_{18} methyl group, the observed NOE on $\text{H}_{7\beta}$ can only be interpreted in terms of an *intermolecular* cholate-cholate NOE arising from an aggregated species. An examination of the perspective diagram of cholate in figure 1 b

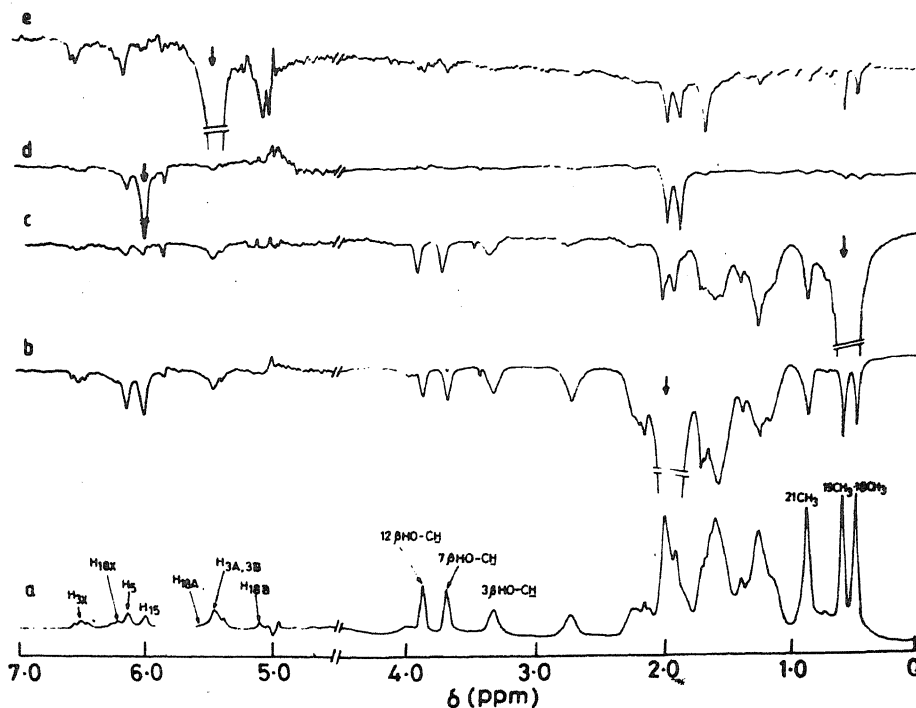


Figure 12. (a) 270 MHz ^1H NMR spectrum of 4:1 cholate-bilirubin. (b-e) Difference NOE spectra obtained upon irradiation of the resonances indicated by an arrow. The difference NOE spectra were obtained as mentioned in the text and are magnified by a factor of 8. (Bilirubin concentration, 30 mM; cholate, 120 mM.)

establishes that the $\text{H}_{7\beta}$ cannot be spatially proximate to either the C_{18} or C_{19} methyl groups. Irradiation of the H_{15} resonance of bilirubin (figure 12d) results in two clear NOE at 1.91 and 2.01 ppm. These correspond to the methyl groups at C_{13} and C_7 of bilirubin. Figure 12e shows the result of an experiment when the olefinic protons on bilirubin, $\text{H}_{18\text{A}}$ and $\text{H}_{3\text{A}}$, were irradiated. Irradiation of these resonances is expected to lead to NOE on the methyl groups at C_2 and C_{17} of bilirubin. In addition rotation of the vinyl group at position 3 can result in an NOE to the C_7 methyl group also. Indeed, NOE to three bilirubin methyl groups are observed at 1.73, 1.91 and 2.01 ppm. A most interesting feature of figure 12e is the observation of NOE on the C_{18} and C_{19} methyl groups of cholate when the $\text{H}_{3\text{A}}$ and $\text{H}_{18\text{A}}$ protons of bilirubin are irradiated. A comparison of figures 12b and 12e clearly shows that this is a selective NOE, since no such effect is observed when H_{15} of bilirubin is irradiated. Thus the spectrum in figure 12e provides clear evidence for an intermolecular interaction between bilirubin and cholate, which brings specific, peripheral olefinic protons into close proximity with the projecting methyl groups on the cholate surface.

All the NOE observed in this study are negative. The magnitudes observed fall in the range 5 to 20%. This suggests that the cholate-bilirubin complex lies in the long correlation limit with $\omega\tau_c > 1$. For molecules of the size of bilirubin or cholate, monomeric species are expected to yield positive NOE at 270 MHz. Indeed

positive NOE have been observed in earlier NMR studies of pure bilirubin in chloroform (Kaplan and Navon 1981) and pure cholate in water below the CMC (S Raghothama, unpublished results). The observation of negative NOE provides further support for the presence of aggregated species in solution for the 4:1 cholate-bilirubin mixture.

4. Discussion

The interaction of bilirubin with bile acids may be monitored by a variety of spectroscopic techniques. As demonstrated in the present study, fluorescence, CD and NMR methods can be useful in probing bilirubin-cholate interactions. While the observation of spectral changes in the presence of bile salts provides support for an intermolecular interaction, the precise nature of the interacting species is less evident. The absence of detectable spectral changes cannot be taken as evidence for the absence of intermolecular interactions.

These features are clearly illustrated by considering the results of the fluorescence and CD studies in conjunction. In the case of cholate a strong enhancement of bilirubin fluorescence is observed at the CMC of cholate (figure 3). The observation of induced CD bands, however, occur at significantly lower cholate concentrations, with appreciable optical activity even at premicellar concentrations (figure 5). In this case it appears that fluorescence enhancements accompany micellar solubilization of bilirubin, whereas induced optical activity results even in the case of presumably low molecular weight complexes. Induced optical activity is also observed upon addition of steroid derivatives like dehydrocholate, which is known to be incapable of micellar aggregation at the concentrations used in this study (Roda *et al* 1983). Deoxycholate, which is known to form micelles at concentrations above 10 mM, causes induced optical activity of bilirubin but does not yield a fluorescence enhancement. It is likely that the nature of cholate and deoxycholate micelles may be different leading to a greater conformational flexibility of the bilirubin molecule in the case of the latter. This could lead to enhanced vibrational deexcitation in the deoxycholate case, resulting in a quenching of fluorescence (Braslavsky *et al* 1983).

The gel permeation studies described earlier afford a means of estimating the size of the micellar complexes under observation and also permit evaluation of the effect of pH on the stability of these complexes. The 1:4 bilirubin-cholate mixture (15 mM bilirubin, 60 mM cholate) used in the gel permeation studies was prepared at pH 10.5, to facilitate dissolution of bilirubin at such high concentrations. Under these conditions, optically clear, intensely absorbing solutions were obtained. Elution profiles were obtained on a Sephadex G-50 column under two distinctly different pH conditions, viz., pH 6.6 and 10.8. The characteristics of the various bilirubin-cholate fractions are summarized in table 2. While two distinct fractions (peaks B and C) are obtained at neutral pH, only one peak (A) is obtained when the elution is performed at alkaline conditions.

Peak A corresponds to a molecular weight of ~ 1780 and from an integration of the ^1H NMR spectrum a cholate to bilirubin stoichiometry of 4:1 is obtained. This species may thus be assigned to a relatively small mixed aggregate composed of approximately 3 to 4 cholate molecules and one bilirubin molecule. Under similar

Table 2. Characterization of bilirubin-cholate complexes obtained by gel permeation.

Frac- tion	Stoichiometry cholate:bilirubin	Estimated molecular weight	CD parameters at different pH values				NOE	
			Acidic $\lambda_{nm}([\theta]_M)^a$	Neutral $\lambda_{nm}([\theta]_M)$	Alkaline $\lambda_{nm}([\theta]_M)$		Intra- molecular	Inter- molecular
Peak A	4:1	~ 1780 (1805-2212) ^b	395(-0.9×10^3); 465(1.1×10^3)	397(-0.5×10^3); 440(0.4×10^3)	c		Observed (negative)	Observed (negative)
Peak B	Cholate $\gg$ bilirubin	≥ 30000	d	430(-2.6×10^3); 480(4.2×10^3)	435(-2.8×10^3); 495(2.5×10^3)		Not determined	Not determined
Peak C	1:2	~ 1120 (1575)	d	397(-1.5×10^3); 490(2.3×10^3)	c		Observed (Negative)	Not (observed)

^a $[\theta]_M$ values as $\text{deg} \cdot \text{cm}^2 \cdot \text{dmol}^{-1}$;

^b values in parentheses correspond to molecular weights for the 3:1 and 4:1 cholate:bilirubin complexes in the case of peak A and the 1:2 complex for peak C;

^c no spectrum observed;

^d not determined.

elution conditions 60 mM cholate eluted at exactly the same position (figure 8). This would correspond to a primary cholate micelle with an aggregation number of approximately 4 to 5. This is in general agreement with estimates of primary micelle size for bile salts which suggest aggregation numbers between 2 and 10 molecules (Carey and Small 1972). It is likely that the mixed aggregate corresponding to peak A results from incorporation of a single bilirubin molecule into the primary micelle. Under the conditions used in this study, a clear resolution of the differences in aggregate size between the pure primary cholate micelle and mixed micelle cannot be made.

The CD spectrum of peak A shows a remarkable sensitivity to the pH of the medium. While characteristic exciton split bilirubin CD profiles are observed at pH 2.4 and 6.7, no induced CD spectrum is detected at alkaline pH. It is likely that in the low molecular weight aggregate, bilirubin is relatively more exposed to the solvent environment at pH 11.4. The absence of CD bands can then be due to conformational flexibility or due to equal populations of both right- and left-handed chiral forms. At lower pH, the structure of the aggregate may be distinctly different with bilirubin now occupying a more sequestered position. Under these conditions, chiral perturbations are more likely to result in an induced CD spectrum. Exactly similar CD behaviour was observed for a 4:1 cholate:bilirubin mixture, which had not been subjected to gel filtration. NOE studies of peak A yielded both intra and intermolecular NOE similar to those described for the 4:1 cholate:bilirubin mixture.

A sudden drop in pH, when the eluant is at pH 6.7, results in a fragmentation of the mixed bilirubin-cholate micelles: A marked pH dependence has also been observed in the bilirubin-human serum albumin case (Brodersen 1982) which has been attributed to the presence of a second type of bilirubin-albumin complex. This complex, which is different from the 1:1 complex, is a large aggregate of bilirubin acid and albumin in molar proportions of about 300:1. Such aggregates can be dissolved on addition of sodium hydroxide, and they leave a 1:1 complex and an excess of bilirubin dianion in solution.

It seems that a similar process is taking place in the bilirubin-cholate case too, with the formation of a 2:1 complex (bilirubin:cholate), and a large complex, which elutes in the void volume of the column and which has very little bilirubin solubilized in a large micellar cholate aggregate.

The stoichiometry of the complex corresponding to peak C is unambiguously established by its proton NMR spectrum (1:2 cholate:bilirubin). The estimated molecular weight of ~ 1120 suggests that this fraction corresponds to a trimeric complex with one cholate and two bilirubin molecules. In this case a characteristic CD spectrum was observed at neutral pH but no optical activity could be detected at alkaline pH. Presumably the trimeric complex readily dissociates at high pH into its individual components. An interesting feature of peak C is the absence of any intermolecular NOE suggesting that the disposition of cholate and bilirubin molecules is appreciably different from that in peak A.

Peak B is undoubtedly a high molecular weight fraction containing a large excess of cholate and can be best described as a micellized bilirubin fraction. In this case induced CD spectra were observed at both neutral and alkaline pH.

In the present study NOE have been used to provide definitive evidence for close intermolecular interactions in the 4:1 cholate:bilirubin system. A particular point

of interest is the observation of relatively large *intramolecular* NOE for both bilirubin and cholate molecules. Earlier studies of bilirubin in organic solvents like chloroform and dimethyl-sulfoxide (Kaplan and Navon 1981, 1982) have yielded limited $\text{NH} \leftrightarrow \text{NH}$ NOE between pyrrole NH protons and $\text{NH} \leftrightarrow \text{CH}$ NOE between pyrrole NH and the bridging methylene protons. In the present study, several NOE have been observed between the olefinic protons of the vinyl group and the bridging methine groups and the peripheral methyl groups. Some of these NOE are in fact conformation sensitive NOE, which provide information about the orientations of the pyrrole groups about the $\text{C}_5\text{--C}_6$ and $\text{C}_{14}\text{--C}_{15}$ single bonds. The observation of these NOE is undoubtedly facilitated by the fact that the complexes have long correlation times, which result in larger magnitudes of the cross relaxation parameters.

A more extensive analysis of the observed NOE together with the CD results may provide a greater insight into the conformations of bilirubin packaged into cholate aggregates.

Acknowledgement

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Microenvironmental differences amongst micelles of various shapes and structures

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Abstract. Micelles of different amphiphiles adopt different shapes and internal packing arrangements in water, depending on their chemical structures and the conditions of the medium. Two microenvironmental features, namely the polarity and the microviscosity that the aggregate offers to a solubilized molecule, have been monitored using extrinsic fluorescence probes. While the differences between micelles of spherical and rod-like shapes are not always distinct, stacked micelles and peptide micelles offer distinctly lower polarity and higher microviscosity to solubilizates than the others.

Keywords. Micellar polarity; micellar microviscosity; shapes of micelles; fluorescence probes; vibronic emission intensity; emission anisotropy.

1. Introduction

A variety of amphiphiles aggregate in water to produce hydrophobic assemblies or micelles. The structure of spherical micelles has recently been reviewed (Gruen 1985). It is however known that micelles can adopt different shapes and internal packing depending on the chemical structures of the constituent monomers. Linear alkyl chain surfactants with an ionic or polar headgroup such as sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB) or *n*-octylglucoside (OG) micellize as spherical particles at low or intermediate concentrations. Ionic micelles such as SDS or CTAB also change their shapes from spherical to rod-like aggregates when the headgroup charge interactions are attenuated by salt addition to the medium (Imae *et al* 1985; Ikeda *et al* 1981). The polyoxyethylene based non-ionic detergent Triton X-100 appears to micellize into oblate ellipsoidal or egg-shaped aggregates (Robson and Dennis 1977). On the other hand the molecular structures of bile salts do not allow them to exhibit the distinct end-to-end polarity which characterizes many aqueous surfactants – but allows them to aggregate at moderate concentrations in water to form micelles. They seem to aggregate as molecular stacks into primary micelles, which further aggregate as secondary micelles at high salt concentrations (Small 1971). Some protein molecules also associate to form hydrophobic assemblies. The surface-active amphiphilic peptide melittin aggregates at high concentrations and in high salt containing aqueous medium to produce tetramers, the crystal structure and solution conformation of which have been determined (Terwilliger and Eisenberg 1982; Brown *et al* 1980). It has been shown that the milk protein κ -casein also forms micellar aggregates (Payens and Vreeman 1982). The cyclic oligosaccharides α -cyclodextrin, β -cyclodextrin and γ -cyclodextrin (cyclohexa-, cyclohepta- and cyclooctaamylose) contain hydrophobic cavities in them which accommodate lipophilic compounds in aqueous solution. Cyclodextrins are not surfactants but are

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considered to be simple models of hydrophobic solubilizers and while both cyclodextrins and surfactant micelles catalyze reactions, the cyclodextrins are simpler and smaller than surfactant micelles. The structure of cyclodextrins is known from x-ray crystallographic analysis (James *et al* 1959).

While all these systems are grossly thought of and used as hydrophobic hosts to incorporate solubilizates, it is of interest to investigate whether they would display features characteristic of their fine structural differences in their sizes or shapes. Some of these features would be the solubilization capacity, the site of localization of the solubilizate and the microenvironment offered by them to the solubilizate in its immediate or cybotactic region (Kosower 1968). Incorporation of polar, polarizable and ionic solubilizates occurs largely around the headgroup region of the host micelles and the microenvironment these solubilizates experience is that of this region (Ganesh *et al* 1982, 1984). Since most micelle-catalyzed reactions involve such solubilizates, it is of interest to monitor the microenvironmental differences, if any, in the solubilization regions of micelles of various sizes and shapes. We present here our attempts to monitor some fine structural differences between micelles of various shapes such as spheres, rods, eggs, stacks, protein aggregates and also the hydrophobic basket-like cavities of α , β - and γ -cyclodextrins. To our knowledge such an attempt has not been made earlier, though the solubilization capacities of spherical and rod-like micelles have recently been compared (Ozeki and Ikeda 1985). The method chosen is the use of different types of fluorescent probes solubilized in host micelles. The spectroscopic probe technique necessarily assumes that the probe molecule does not perturb the local environment or structure. Usually this is hopefully ascertained by choosing a very low probe:surfactant mole ratio such that most micelles are 'free', several micelles are singly housed with the probe and only a negligible number of micelles are doubly occupied, following the Poisson distribution. Such a situation obtains when fluorescent probes are used wherein micromolar concentrations of probes are used with decimolar surfactants, and the sensitivity of the fluorescence method allows this low probe:surfactant ratio. The principle behind this technique is that it utilizes the changes in the fluorescence of the electronically excited probe molecule to elucidate specific properties of the host system such as its polarity and fluidity. Fluorescence probes used in micellar systems can also be used in biological systems such as membranes, liposomes and proteins.

The fluorescence spectrum of the neutral arene molecule pyrene has been used to monitor the medium polarity. The relative intensity ratio of the third and the first vibronic components I_3/I_1 (the so-called Ham effect) of the emission spectrum of pyrene is a measure of the polarity experienced by the probe molecule around its environment (Nakajima 1976). 8-Anilino-1-naphthalene sulphonic acid (magnesium salt) (ANSA) is another probe whose fluorescence emission wavelength ($\lambda_{\max}$) and intensity (I_f) are indicative of the polarity of the environment surrounding it (Stryer 1968). Diphenyl hexatriene (DPH) is a fluorescence probe whose emission quantum yield gets enhanced upon incorporation from water into a micelle. In addition the fluorescence polarization (P) and anisotropy (r) of DPH allows us to estimate the microviscosity (η) of the medium in which the fluorophore is placed (Shinitzky and Barenholz 1978). DPH has been used in our studies to monitor, through its anisotropy, the microviscosity of the host micellar systems. Zachariasse *et al* (1982) have introduced a very useful probe, (dipyrenyl)-methyl

ether (DPME). This molecule displays the Ham effect in its emission around 370–400 nm (the monomer emission) and also forms an intramolecular excimer whose emission is a broad band around 450 nm. The efficiency of excimer formation is directly governed by the fluidity of the medium. Thus the relative intensity ratio of the excimer band to that of the monomer band, I_e/I_m , is an index of the microviscosity of the medium; the higher the microviscosity the lower the ratio. In addition, the vibronic band ratio I_3/I_1 of the monomer emission is sensitive to the polarity of the medium. We have used this two-in-one probe to monitor several micellar systems.

2. Experimental section

Sodium dodecylsulphate (SDS, from Biorad) was recrystallized twice from ethanol. Cetyltrimethylammonium bromide (CTAB), sodium deoxycholate, sodium cholate, pyrene, DPH and ANSA were obtained from Sigma and used without further purification. Cetyltrimethylammonium chloride (CTAC) was made in the laboratory from CTAB by extensive dialysis using sodium chloride. Melittin (Serva), α -, β -, γ -cyclodextrin (Aldrich) and CHAPSO (a zwitterionic detergent 3-[3-(cholamidopropyl)-dimethyl-ammonio-]-2-hydroxy-1-propanesulphonate) (Calbiochem) were used as such. κ -casein was isolated from milk and purified by HPLC. (Dipyrenyl)-methyl ether was a gift from Dr K A Zachariasse. Stock solutions of pyrene, DPME and ANSA were made in methanol, while that of DPH was made in tetrahydrofuran (distilled and passed over an alumina column). The concentration of the probes pyrene, DPME and DPH was 1 μ M in each micelle solution, whereas in the case of ANSA we have used 10 μ M. We have taken care to see that the probe to micelle ratio is as low as 1:100 so that the probe perturbs the micellar structure only negligibly. Direct addition of an organic solution of the probe to water leads to the formation of microcrystals that are responsible for low fluorescence intensities. This can be avoided by extensive sonication and incubation. The sample solutions were made and kept for incubation for 8–10 hrs before recording their fluorescence spectra. The fluorescence signal of systems containing DPH decreases with time on exposure to the excitation light. Upon shutting off the excitation light for periods of 15–30 seconds the system regains its original fluorescence signal. The phenomenon, which originates from reversible photoisomerization of DPH, was eliminated by reducing the period of exposure to excitation light to less than 10 seconds so as to ensure that it is in the all *trans* form.

Fluorescence spectra were measured using a Hitachi 650-10S instrument (at 297 K). The excitation wavelengths for pyrene, DPME, ANSA and DPH were 334, 335, 365 and 357 nm, respectively. Fluorescence polarization (P) and anisotropy (r) values were calculated from the intensities obtained at 0–0°, 0–90°, 90–90° and 90–0° angle settings of the excitation and emission polarizers respectively and using a correction factor for I (Azzi 1974). Microviscosities were calculated using standard equations (Shinitzky and Barenholz 1978). The polarities were estimated using the pyrene band ratio values measured in methanol:water and methanol:*n*-octanol mixtures of varying volume ratios, using the same instrument and experimental conditions. The polarities of the host systems are thus compared to those of aqueous methanol or methanol:octanol mixtures.

3. Results and discussion

The fluorescence intensities of the several vibronic fine structures in the pyrene monomer fluorescence show strong solvent dependence. The strong perturbation in the vibronic band intensities of pyrene is more dependent on the solvent dipole moment than on the bulk solvent dielectric constant (Dong and Winnick 1982). The strong perturbation of the vibronic band intensities has been used as a probe to determine the polarity of the medium surrounding pyrene. Out of the five vibronic bands exhibited by pyrene emission in the 365–400 nm region, the vibronic component peak 3 shows the maximum variation in intensity relative to that of the 0–0 band (peak 1). Hence the relative intensity of peak 3 to that of peak 1, referred to as the I_3/I_1 ratio, is used here to monitor the environmental effects of micelles on pyrene monomer fluorescence. The peak ratios are quite reproducible (± 0.02). The sharpness of the five vibronic frequencies as well as the I_3/I_1 ratio increase as one goes through a series of simple polar solvents, (the ratio ranges from 0.5 to 0.8) aromatic solvents (0.8 to 1.0), hydrocarbon solvents (around 1.6 to 1.8) and saturated perfluorocarbon solvents where it is around 2.

Dong and Winnick (1982) have analyzed the vibronic intensity ratio of pyrene emission in a variety of homogenous media and attempted to correlate those with the empirical solvent polarity parameters E_T^{30} (Reichardt and Dimroth 1968) and their own P_y values. Kalyanasundaram and Thomas (1977) have measured the pyrene emission ratio I_3/I_1 in micellar systems. We have used 1 μ M pyrene as a solubilize in a variety of host micelles, proteins and cyclodextrins and monitored its I_3/I_1 emission ratios in these. As with other aromatic solubilizes reported earlier (Ganesh *et al* 1982, 1984), pyrene is expected to be solubilized and located largely in the headgroup region of the host micelles and would report on the polarity of this region. Table 1 lists the results obtained in such a study in several systems using pyrene, and estimates the polarities in terms of comparable homogeneous solvents and solvent mixtures. The polarity experienced by pyrene decreases from water in the order α -cyclodextrin, casein micelles, the egg-shaped micelles of Triton X-100, CTAB micelles, SDS micelles, melittin tetramers – the least polar being the stacked micelles of the bile salts and their derivatives.

We wish to comment in passing about the suggestion (Dong and Winnick 1982) that in anisotropic systems we might see differences in the Ham effects of the absorption and emission spectra of pyrene. The rationale behind this argument is that such a difference would imply a net change in the environment of the excited pyrene subsequent to absorbing a photon and prior to emitting a photon. Accordingly we measured the extinction coefficient ratio $\epsilon_{362}/\epsilon_{377}$ values of pyrene in spherical, rod-like, egg-shaped and stacked micelles and compared them with the I_3/I_1 emission ratio in the corresponding system. In all these cases the former was uniformly found to be about twice the value of the latter and no distinction was discernible based on the shape of the host aggregate.

The emission quantum yield and the wavelength maximum of the fluorescence of ANSA have also been used to monitor the polarity of the medium surrounding this fluorophore molecule (Stryer 1968). The wavelength of maximum emission reflects the overall dipolar character of the solvent, whereas Q is sensitive to more localized deactivating processes. Of the two parameters we have chosen to limit our attention to λ_{max} since the intensities of emission of this anionic probe could vary

Table 1. Polarity of host assemblies monitored by pyrene and by ANSA.

System	Pyrene I_3/I_1^*	$\lambda_{\max}$ ANSA ^{**} , nm	Remarks on polarity
Water	0.58	515	
<i>Apolar cavities</i>			
α -Cyclodextrin	0.59	495	water
β -Cyclodextrin	1.07	495	30% MeOH in octanol
<i>Spherical micelles</i>			
SDS, 25 mM	0.92	490	95% MeOH 5% octanol
CTAB, 25 mM	0.79	485	35% MeOH 65% water
<i>Rod-like micelles</i>			
SDS + NaCl	1.01	490	55% MeOH 45% octanol
CTAB + NaBr	0.80	480	30% MeOH 70% water
<i>Egg-shaped micelles</i>			
Triton X-100, 10 mM	0.74	485	50% aq. methanol
<i>Stacked micelles</i>			
Na DOC, 10 mM	1.37	490	<i>n</i> -butyl ether (?)
Na DOC + NaCl	1.44		
Na cholate, 10 mM			
Na cholate + NaCl	1.22	48	<i>n</i> -butyl ether (?)
CHAPSO, 10 mM	1.13	475	neat octanol
<i>Peptide micelles</i>			
Melittin tetramers	1.06	465	35% MeOH 65% octanol
Casein micelles	0.6	470	water

* 1 μ M pyrene, excited at 334 nm, slit width 5 nm, 1 cm cell, room temperature (297 K).

** 10 μ M ANSA, excited at 365 nm, slit width 5 nm, 1 cm cell, room temperature (297 K).

depending upon the coulombic interactions with the headgroup charges of the host micelles and the extent of partitioning and solubilization in them. Being aromatic and charged, ANSA would be expected to be solubilized not in the core of the host micelle but near the headgroup region and thus report on the polarity of this region (Ganesh *et al* 1982, 1984). Table 1 compares the $\lambda_{\max}$ of ANSA in a variety of micelles with trends that are roughly the same as those obtained with the other probe pyrene.

ANSA reports the polarities of the cyclodextrin hydrophobic cavities to be higher than any of the micelles we have studied. The polarity of both the cavities is seen to be roughly that of 10% dioxane in water. It is possible that ANSA does not accommodate itself well into either of the cavities. The rod-like micelles appear to display slightly reduced polarities than spherical ones. The stacked micelles offer the least polar environment that is accentuated further in secondary micelles of the bile salts in high salt media.

The results on polarities obtained using ANSA are not identical with those using pyrene, which is not surprising in the light of the different mechanisms that operate in the two cases. But the general trend that emerges out of such polarity probing is that the polarity of the microenvironment decreases in order: cyclodextrin cavities are the most polar, then are the spherical, egg-shaped and rod-like micelles, and

the least polar of the surfactant micelles being the stacked assemblies. The peptide micelles of melittin tetramers and of the protein casein offer the least polar environment of all for ANSA, though pyrene sees them to be more polar than bile salt micelles. This difference in the behaviour of ANSA and pyrene in the proteins might perhaps be due to differences in their binding sites, a point that needs to be established.

It is important to reiterate that the polarity being studied is not that of the interior or the core of the micelle, but that of the region near the headgroup or at best a few methylenes beneath. The polarity of the core would be roughly that of a liquid alkane in spherical micelles, as the standard picture implies (Gruen 1985). Any probe that is used, being polar or polarizable as ANSA and pyrene are, would tend to locate itself largely near the headgroup region of the host micelle and would report on its immediate or cybotactic region. It is thus of interest to note that even in this region, cyclodextrin cavities, spherical and rod-like micelles differ in their polarity features from stacked micelles, and from protein micelles. While the polarity difference between spherical and rod-like micelles is not substantial, it is so in bile salt micelles.

The other parameter of interest is the microenvironmental viscosity or the microviscosity of the micellar aggregate. This can be estimated (Shinitzky and Barenholz 1978) by using the fluorescence anisotropy or polarization of the probe diphenylhexatriene (DPH). Table 2 summarises the anisotropy values and the environmental microviscosity estimates in a variety of systems. The emission intensity increases perceptibly upon incorporating the DPH into host systems, though no definite shape-dependent trends emerge. This at least in part is due to the variation seen in the intensity upon changing the detergent concentration, since we cannot use the same number of molecules of the detergent in the micelle in each case. The microviscosities we have measured agree for CTAB spheres and for Triton X-100 micelles with those reported using other probes, around 50 cP for CTAB (Blatt *et al* 1982) and by 145 cP for Triton X-100 (Watkins and Selinger 1979).

The estimated microviscosities increase in the general order: spherical micelles, α -cyclodextrin, rod-like micelles, egg-shaped micelles, β -cyclodextrin, melittin tetramer, the most viscous being the stacked micelles of bile salts. One would also expect DPH to be intercalated within the stacks of the bile salt micelles leading to the greater degree of immobilization that is seen here. In comparison, its binding to the hydrophobic patch of melittin tetramers or the rod-like micelles would offer it higher mobility. It is interesting however that Triton X-100 micelles seem to immobilize DPH better than rod-like micelles. One must however add here that the only example of an egg-shaped micelle we have is that of polyoxyethylene-based Triton X-100. Whether the increased microviscosity seen by DPH here is due to the inherent packing mode of the micelle or to the influence of polyoxyethylene, a known medium of higher viscosity, is not clear. The other polyoxyethylene-based nonionic detergent, Brij 35, whose shape is not known yet, appears to be four times more viscous than Triton X-100. In any event, it is seen that microviscosity differences between the various assemblies seem to be more marked and better distinguishable than their polarity differences.

The composite probe (dipyrenyl)-methyl ether (DPME) displays not only the emission bands of the constituent pyrene moieties with their vibronic fine structure

Table 2. Fluorescence features of diphenylhexatriene (DPH)* solubilized in various media.

System	Intensity (a.u.)	Anisotropy (<i>r</i>)	Microviscosity (poise)
Water	2.5		
<i>Spherical micelles</i>			
SDS, 25 mM	50.4	0.080	0.66
CTAB, 25 mM	443	0.072	0.58
<i>Rod-like micelles</i>			
SDS + NaCl	208	0.094	0.82
CTAB + NaBr	376	0.078	0.77
<i>Egg-shaped micelles</i>			
Triton X-100, 10 mM	470	0.116	1.11
<i>Peptide micelles</i>			
Melittin tetramers	462	0.191	2.64
<i>Stacked micelles</i>			
Na DOC	220	0.228	4.03
Na cholate	203	0.263	6.26
CHAPSO	162	0.102	1.05
<i>Apolar cavities</i>			
α -Cyclodextrin	35	0.081	0.68
β -Cyclodextrin	56	0.172	2.15

*DPH = 1 μ M in THF excited at 357 nm, emission at 430 nm, ambient temperature (297 K); 1 cm cell, slit width 4 nm. Solution kept in dark for 30 s prior to measurement so as to ensure that the probe is exclusively in the *trans* isomeric form. The estimated values of $\bar{\eta}$ are accurate to $\pm 15\%$.

(monomer fluorescence), but also an intramolecular excimer emission band beyond 450 nm. The vibronic intensity ratio of the monomer fluorescence of DPME monitors the polarity of the medium just as the I_3/I_1 ratio of pyrene itself does. In addition, the intensity ratio of the excimer band to that of the monomer band (I_e/I_m) depends on the viscosity of the environment of DPME; the higher the environmental viscosity (or microviscosity of the host aggregate in which DPME is incorporated), the lower the excimer: monomer intensity ratio I_e/I_m (Zachariasse *et al* 1978; Zachariasse 1986). Use of DPME might be advantageous in comparison to the use of separate probes to measure the polarity (pyrene, ANSA) and the microviscosity (DPH) of host assemblies. It is more frequently used to compare the relative microviscosities or fluidities of the same assembly under different conditions.

Table 3 presents the results on the polarity and microviscosity profiles of several of the test assemblies, using DPME as the composite probe in them. It is to be pointed out that the vibronic ratios obtained using DPME need not be the same as those with pyrene itself, due to the fact that the two molecules differ in structure (the I_3/I_1 ratios for DPME and for pyrene in water are 0.71 and 0.58 respectively) and also the possibility that the two probes may not be located in identical regions of the host assembly (DPME gives a value of 0.59 in β -cyclodextrin while with

Table 3. Fluorescence features of DPME* in various assemblies.

System	I_3/I_1 monomer band	I_e/I_m
<i>Apolar cavities</i>		
α -Cyclodextrin	—	—
β -Cyclodextrin	0.59	—
γ -Cyclodextrin	0.84	0.13
<i>Spherical micelles</i>		
SDS, 25 mM	0.57	0.32
CTAC, 25 mM	0.67	0.33
<i>Rod-like micelles</i>		
SDS + NaCl	0.66	0.38
CTAC + NaCl	0.67	0.28
<i>Egg-shaped micelles</i>		
Triton X-100, 10 mM	0.73	0.21
<i>Stacked micelles</i>		
Na cholate, 10 mM	0.84	0.13
Na DOC, 10 mM	0.94	0.17
Na cholate + NaCl	0.92	0.25
Na DOC + NaCl	1.16	0.07
<i>Peptide micelles</i>		
Melittin tetramers	1.07	0.66

*1 μ M DPME; excited at 335 nm, emission of monomer band in the 370–400 nm region and of the intramolecular excimer band above 450 nm; 1 cm cell; slit width, 4 nm; ambient temperature (297 K).

pyrene it is 1.07). Yet the trend seen in the polarity profile of these systems is largely the same as with pyrene. DPME was not found to be solubilized in α -cyclodextrin solutions, perhaps because of its size. Even in β - and γ -cyclodextrins, it seems to be accommodated only partially. The excimer band of DPME could not be measured in the former, and it also has a smaller intensity compared to that of the monomer band in the latter.

The excimer: monomer emission ratios, I_e/I_m , of DPME in these systems is only partly in line with those expected based on their microviscosities measured by DPH, and there are exceptions. For example, the microviscosity of the DPH binding site in melittin tetramers is more than that of Triton X-100. Yet the I_e/I_m ratio of DPME in melittin is the highest amongst all the systems studied. Similarly there is a substantial increase in the excimer emission of DPME in SDS rods compared to that in SDS spheres, and in the cholate secondary micelles as compared to its primary micelles. In DPME, the intensity of the monomer emission is sensitive to the medium polarity while that of the excimer band is not. Thus there would be variations in the I_e/I_m ratios that depend not only on the microviscosity but on the polarity of the medium as well. This would be responsible for the differential responses of DPME and of DPH to medium microviscosities.

4. Conclusions

In conclusion, it appears possible by fluorescence probe methods to monitor the microenvironmental differences amongst micelles of different shapes. The caveat is that the environment being monitored is not the micellar core but the region a little beneath the headgroup (since that is largely where most polar and polarizable probes are solubilized in micelles). Even in this region of different micelles, the polarity and the microviscosity differ in different systems. The polarity appears to decrease in the order – cyclodextrin cavities, spherical and rod-like ionic micelles, bile salt micelles and protein self-aggregates. The fluidity of the medium surrounding solubilized DPH appears to decrease in the order – spherical micelles, rod-like micelles, egg-shaped micelles, melittin micelles, with the bile salt stacks offering the most microviscous environment for DPH.

Clear differences arise between stacked micelles on the one hand and other micelles of surfactants on the other. It would be interesting to try the fluorescence approach to predict the possible shape of aggregates whose shapes are not known. Aggregates of surface-active or membrane-active peptides and proteins could also be analyzed using this approach.

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Role of the hydrophobic region of signal sequences in the targeting of proteins to membranes and translocation across the hydrophobic membrane barrier

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Abstract. Proteins destined for regions other than the cytoplasm in cells have to cross at least one membrane barrier before reaching their proper destination. Almost all such proteins are initially biosynthesized as precursors with signal sequences at the amino terminus. Signal sequences are essential and also sufficient for proteins to be targeted to membranes and also for translocation across membranes. One striking feature that is clearly evident amongst signal sequences of secretory proteins is a positively charged amino terminus followed by a region comprising 10-12 very hydrophobic amino acids. The structural and physico-chemical properties of signal sequences have been analysed. On the basis of the analyses it is proposed that the structural feature of a positively charged amino terminal region followed by a hydrophobic stretch of amino acids, rather than a conformational one, is recognised by components of the cells export machinery. It is also postulated that signal sequences insert in the lipid bilayer of the translocation competent membrane after targeting. The presence of the signal sequence results in the formation of local 'defects' in the bilayer which have a role in translocation of proteins across membranes.

Keywords. Signal sequence; hydrophobicity; targeting to membranes; translocation across membranes; signal sequence receptors; signal-sequence membrane interactions.

1. Introduction

Proteins destined for regions other than the cytoplasm in cells have to cross at least one membrane barrier before reaching their proper destination. Almost all such proteins are initially biosynthesized as precursors with signal sequences at the amino terminus (Kreil 1981; Michaelis and Beckwith 1982; Hay *et al* 1984). Peptidases present in the endoplasmic reticulum, the inner membrane in *E. coli* (Wolfe *et al* 1983) and in the matrix space in mitochondria (Boehni *et al* 1980) cleave off the signal sequences from the precursor proteins. Gene fusion and *in vitro* reconstitution experiments indicate that signal sequences are essential and also sufficient for proteins to be targeted to the appropriate membrane site (endoplasmic reticulum and mitochondria in eukaryotes and inner membrane in prokaryotes) and also translocation across these membranes (Lingappa *et al* 1984; Horwich *et al* 1984, Van Loon *et al* 1986; Perara and Lingappa 1985).

The primary structures of a large number of signal sequences have been determined and compiled recently (Watson 1984). Interestingly, there is no primary structure homology amongst signal sequences. However, one striking feature is clearly evident amongst signal sequences of secretory proteins. All of them have a positively charged amino terminus region followed by a region comprising 10-12 very hydrophobic amino acids like Leu, Ile, Val, Phe. There is

considerable evidence that the hydrophobic region is essential for signal sequences to be able to initiate export of proteins efficiently (Benson and Silhavy 1983; Lee and Beckwith 1986). This article analyses the structural and physico-chemical properties of signal sequences destined for secretion and attempts to answer the two following questions:

- (1) Is it the hydrophobic region in signal sequences that is recognized by components of the cells export machinery?
- (2) What is the role of the hydrophobic region in the ability of signal sequences to initiate translocation of proteins across membranes?

2. The hydrophobic nature of signal sequences

The primary structures of some representative signal sequences and a schematic sketch of the distribution of amino acids is shown in figure 1. All signal sequences (Watson 1984) have one or two positively charged amino acids in the amino terminal region, approximately 5-residue long. This is followed by a stretch of highly hydrophobic amino acids like Leu, Ile, Val or Phe. The carboxy terminal region amino acids have short side chains like Gly, Ala, Ser or Cys. Signal sequences have been analysed with respect to the mean hydrophobicity at each position in the peptide segment (von Heijne 1982). The analysis reveals a non-uniform hydrophobic distribution with maximum hydrophobicity at the mid-point of the peptide segment. This distribution was not observed in the hydrophobic regions of intrinsic membrane proteins.

The total hydrophobic contribution to the free energy of interaction between signal sequences and the hydrophobic interior of membranes have been computed (von Heijne 1981, 1985; Engelman and Steitz 1981). A free energy of ~ 120 kJ/mol was obtained indicating that the signal sequences would spontaneously partition into the hydrophobic interior of membranes.

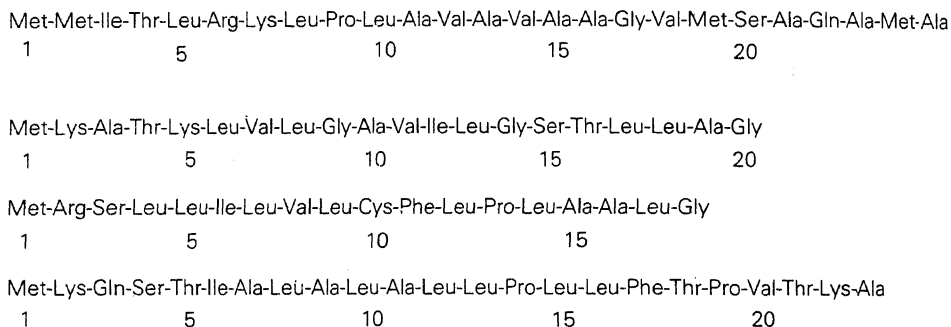


Figure 1. Primary structures of some representative signal sequences. The areas A, B and C in the line diagram correspond to the positively charged amino terminal (~ 5 amino acids), hydrophobic core segment (~ 10 – 15 amino acids) and carboxy terminal (~ 6 amino acids) regions. The sequences have been taken from Watson (1984).

3. Conformations of signal sequences

The conformations of several signal sequences have been analysed by the method of Chou and Fasman (Austen 1979). However, a common conformational feature does not emerge from this analysis. The conformations of some synthetic signal peptides have been studied by circular dichroism (CD) spectroscopy (Rosenblatt *et al* 1980; Briggs and Gierasch 1984; Shinnar and Kaiser 1984; Katakai and Iizuka 1984; Laxma Reddy and Nagaraj 1985, 1986). In aqueous or polar environments, the peptides studied had very little ordered conformation. In hydrophobic environments the peptides adopted ordered conformations. Exclusively α -helical conformations were observed for 3 signal sequences (Rosenblatt *et al* 1980; Shinnar and Kaiser 1984; Laxma Reddy and Nagaraj 1985). One signal sequence showed both α -helical and β -sheet conformations (Laxma Reddy and Nagaraj 1986). The conformations of shorter fragments of signal sequences have also been studied (Briggs and Gierasch 1984; Katakai and Iizuka 1984; Laxma Reddy and Nagaraj 1985). The amino terminal regions were found to be unordered whereas the central hydrophobic portion adopted α -helical conformations.

Recently the conformations of a signal peptide induced by lipids have been studied (Briggs *et al* 1986). When the signal peptide was bound only to the charged head groups of phospholipids, a β -sheet conformation was observed. Under experimental conditions in which the peptide was associated with the hydrocarbon region of phospholipids, an α -helical conformation was discernible.

4. Features in signal sequences essential for proper sorting of proteins

Extensive genetic studies in *E. coli* (Benson and Silhavy 1983; Lee and Beckwith 1986) have indicated how mutations resulting in change or deletion of amino acids in the amino terminal and the hydrophobic regions of signal sequences affect their ability to initiate the export of proteins. Figure 2 shows the effect of changes in the amino terminus of the signal sequence of *E. coli* lipoprotein (Inouye *et al* 1982;

Wild type	Charge	
Met-Lys-Ala-Thr-Lys-Leu	+2	
Met-Lys-Ala-Thr-Asn-Leu	+1	
Met-Ala-Thr-Asn-Leu	0	
Met-Glu-Asp-Thr-Asn-Leu	-2	non functional
Met-Lys-Asp-Thr-Lys-Leu	+1	
Met-Ala-Thr-Lys-Leu	+1	
Met-Asp-Thr-Lys	0	non functional
Met-Glu-Asp-Thr-Lys	-1	

Figure 2. Amino terminal region of the wild type and mutant signal sequences of *E. coli* lipoprotein (Inouye *et al* 1982; Vlasuk *et al* 1983). The amino acids replaced by mutation are italicized.

E. coli alkaline phosphatase:

Met-Lys-Gln-Ser-Thr-Ile-Ala-Leu-Ala-Leu-Leu-Pro-Leu-Leu-Phe-Thr-Pro-Val-Thr-Lys-Ala
1 5 10 15 20
Glu His

Met-Lys-Ile-Thr-Gly-Ala-Arg-Ile-Leu-Ala-Leu-Ser-Ala-Leu-Thr-Thr-Met-Met-Phe-Ser-Ala
1 5 10 15 20
↓ ↓
Glu Lys

Met-Lys-Ala-Thr-Lys-Leu-Val-Leu-Gly-Ala-Val-Ile-Leu-Gly-Ser-Thr-Leu-Leu-Ala-Gly
1 5 10 15 20
↓
Asp

Met-Met-Ile-Thr-Leu-Arg-Lys-Leu-Pro-Leu-Ala-Val-Ala-Val-Ala-Ala-Gly-Val-Met-Ser-Ala-Gln-Ala-Met-Ala
1 5 10 15 20 25

↓ Asp ↓ Gln Arg/Ly

deletion mutant

Met-Met-Ile-Thr-Leu-Arg-Lys-Leu-Leu-Pro-1
1 5

R1 Met-Met-Ile-Thr-Leu-Arg-Lys-Leu-Pro-1
1 5

R2 Met-Met-Ile-Thr-Leu-Arg-Lys-Leu-Leu-1
1 5

1-Val-Ala-Ala-Gly-Val-Met-Ser-Ala-Gln-Ala-Met-Aln
15 20 25

1-Val-Ala-Ala-Cys-Val-Met-Ser-Ala-Gln-Ala-Met-Ala
15 20 25

1-Val-Ala-Ala-Gly-Val-Met-Ser-Aln-Gln-Ala-Met-Ala
15 20 25

Figure 3. Wild-type and mutant signal sequences of some *E. coli* proteins. Changes as a result of mutation are indicated by arrows (↓) indicates that the mutational change results in a defective signal sequence that cannot initiate export of proteins. (↘) indicates that the mutational change does *not* result in a defective signal sequence. R1 and R2 are pseudo revertant sequences. The alkaline phosphatase wild type and mutant signal sequences are from Michaelis *et al* (1986). The wild type and mutant maltose binding protein, lipoprotein and λ-receptor sequences are from Benson and Silhavy (1983). The deletion mutant and pseudo revertant signal sequences of λ-receptor are from Emr and Silhavy (1983).

proteins is depicted. Mutant signal sequences in which a charged residue is present in the hydrophobic region resulting in the *reduction* of the length of the hydrophobic stretch are non-functional. In pseudo-revertant signal sequences, the reduction of length of the hydrophobic stretch in mutants is removed, resulting in functional signal sequences. Deletions of hydrophobic amino acids also render signal sequences non-functional. In the case of the *E. coli* λ -receptor 'wild-type' mutant and pseudo-revertant signal sequences (Emr and Silhavy 1983) the observations have been rationalized in terms of the conformation of these sequences. Peptides corresponding to these sequences were synthesized and their secondary structures analysed by circular dichroism spectroscopy (Briggs and Gierasch 1984). An α -helical conformation was observed only in the 'wild-type' and pseudo-revertant sequences, whereas the deletion mutant sequence was largely unordered. Hence it was concluded that an α -helical conformation in the central hydrophobic region is essential for the function of signal sequences. It is likely that a positively charged amino terminus and a 'critical size' of the hydrophobic region is essential for eukaryotic signals as well. In fact it has been demonstrated that replacement of Leu by its polar analog β -hydroxy leucine renders a eukaryotic signal sequence non-functional (Hortin and Boime 1980).

5. Targeting of proteins destined for secretion to the membrane site

Extensive biochemical studies particularly *in vitro* reconstitution experiments in eukaryotes have shown how ribosomes synthesizing secretory proteins are targeted to the endoplasmic reticulum (Walter *et al* 1984; Walter and Lingappa 1986). A protein-RNA complex, the signal recognition particle (SRP), recognizes and binds to the signal sequence of the secretory protein as it emerges from the ribosome. This binding results in the arrest of translation of the secretory protein from its m-RNA. The SRP-nascent secretory protein-ribosome complex then moves to the endoplasmic reticulum where SRP binds to its 'receptor', the docking protein. Thus binding results in the release of translation arrest. Although molecules like SRP and docking protein have not been characterized in prokaryotes, several genetic loci that may specify components of the cellular export machinery have been identified (Benson *et al* 1985). While it is not clear whether regions other than the signal sequence are recognized by SRP in precursor proteins, the presence of the signal sequence is essential for SRP induced translation arrest. Removal of the signal sequence of pre-pro-insulin by recombinant DNA techniques abolished interaction between the polypeptide and SRP (Weidmann *et al* 1986) indicating the absolute requirement of signal sequence for recognition by SRP.

6. Translocation of proteins across membranes

Once targeting to the membrane site is accomplished the next step is translocation of proteins across the hydrophobic membrane barrier. Widely differing views as to how this happens exist. According to one school (Inouye and Halegoua 1979; Engelman and Steitz 1981; von Heijne 1985) translocation is initiated by spontaneous partitioning of the signal sequence into the lipid bilayer of membranes. This is followed by the rest of the polypeptide chain. There is no direct

experimental evidence supporting this view. Recently *E. coli* precursor proteins have been shown to translocate across membrane vesicles comprising only phospholipids (Geller and Wickner 1985). It would be of interest to examine whether precursor secretory proteins of eukaryotes can be translocated across a model membrane system devoid of proteins.

Another school favours translocation through a protein channel in the membrane (Walter *et al* 1984; Singer *et al* 1987). Translocation is initiated by binding of the signal sequence to the protein which results in the opening of an aqueous protein channel in the membrane. However no such protein or proteins have been identified so far.

7. The role of the hydrophobic region in signal sequences in targeting of proteins to the translocation competent membrane and in transfer of proteins across such membranes

A positively charged amino terminus followed by a stretch of at least 7–8 hydrophobic amino acids is absolutely essential for a signal sequence to be able to initiate the export of proteins. Any change in these regions which alters the charge or reduces the length of the hydrophobic stretch results in defective signal sequences. The conformations that signal sequences adopt are clearly environment dependent and both α -helical and β -sheet conformations are observed. Hence, I feel that it is the structural feature of positively charged amino terminus followed by a hydrophobic region that is recognized by components of the cells export machinery. An α -helical conformation may not be as stringent a requirement as the distribution of charged and hydrophobic amino acids for recognition.

The role of signal sequences in initiating translocation of proteins across membranes differs widely in the models that have been proposed to explain this step. In the 'direct transfer' models, translocation is initiated by spontaneous partitioning of signal sequences in the hydrophobic interior of membranes, whereas in models where translocation is postulated to occur through protein channels, the signal sequences interact with a protein receptor in the membrane. In any event, it is the initial interaction of signal sequences with membranes that opens up a pathway for translocation, as these sequences are cleaved off precursor proteins by membrane-bound signal peptidases before the translocation of the entire protein across membranes is completed. We (Nagaraj 1984; Nagaraj *et al* 1987) and some others (Briggs *et al* 1985, 1986) have studied the interaction of synthetic signal peptides with model membranes and have observed that these peptides partition spontaneously into the lipid bilayer. We have also demonstrated that the association of signal sequences with model membranes results in extensive perturbation of the lipid bilayer (Nagaraj *et al* 1987). Taking these results into account and also the observation that some precursor proteins can translocate across the lipid-bilayer of membrane vesicles devoid of proteins, I propose that *in vivo*, signal sequences insert into the lipid bilayer of the translocation competent membrane after targeting to the membrane site has occurred. The presence of the signal sequence results in the formation of 'local defects' in the lipid bilayer. Translocation of the mature portion of the protein can then conceivably occur through 'defects' in the lipid bilayer. Alternatively, the perturbation of the lipid

bilayer could result in the rearrangement of membrane proteins so as to open up aqueous channels for translocation.

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